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Technical Report S-123

THERMAL STABILITY OF SOME NF PROPELLANTS (U)

by

E. L. Allen

December 1967

U. S. ARMY MISSILE COMMAND
Redstone Arsenal, Alabama 35809

Contracts
DA-01-021-AMC-11536(Z)
DAAH01-67-C-0655

ROHM AND HAAS COMPANY
REDSTONE RESEARCH LABORATORIES
HUNTSVILLE, ALABAMA 35807

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December 1967

Technical Report S-126

THERMAL STABILITY OF SOME NF PROPELLANTS (U)

by

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E. L. Allen

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(U) FOREWORD

The work described in this report was performed under Contracts DA-01-021-AMC-11536(Z) and DAAH01-67-C-0655 for exploratory development of propellants for missiles and rockets under the cognizance of the Solid Propellant Chemistry Branch, Army Propulsion Laboratory and Center, Research and Development Directorate, U. S. Army Missile Command.

All sections of this report which contain propellant formulations or thermal stability data for NF compositions are classified Confidential. Sections dealing exclusively with test methods are unclassified.

Throughout the development and scale-up program for NF propellants, major contributions toward evaluating and improving thermal stability have been made by many individuals. With Dr. T. E. Stonecypher—and more recently, Mr. D. A. Willoughby—as group leader, the Applied Thermodynamics Group in the Engineering Research Section has been involved continuously for the past three years in the study of thermal stability. The success of these efforts, however, would have been impossible without the suggestions and cooperation of other groups within these Laboratories. The author particularly acknowledges the contributions and assistance of Dr. B. F. Aycock, Dr. M. G. Baldwin, Mr. D. W. Booth, Mr. E. D. Bosserman, Mr. J. L. Chaille, Mr. C. E. Cutchens, Mr. P. H. Gehlhaus, Mr. W. H. Groetzinger, III, Dr. A. J. Ignatowski, Dr. F. A. Johnson, Dr. K. E. Johnson, Mr. R. L. Johnson, Mr. R. E. Lide, Mr. B. R. Minton, Mr. B. K. Nipp, Mr. J. W. Parrott, the late Dr. R. C. Petry, Mr. K. Scroggum, Mr. R. D. Shoults, Mr. T. L. Willetts, and Dr. R. S. Yost. In addition, the capable assistance of Mr. J. F. McKinney in performing the adiabatic decomposition and fissuring tests has added immeasurably to the quality and quantity of the experimental program.

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(C) ABSTRACT

(C) The efforts of these Laboratories in evaluating and improving the thermal stability of high energy NF propellants based on NFPA and TVOPA are summarized. Test methods are briefly described. Sufficient experimental results are included to demonstrate significant improvements which were achieved. Methods which led to these improvements are described; these include the use of an acrylic acid-diepoxy curing system, purification of TVOPA in an ion-exchange column, inclusion of Alon-C¹ (finely divided aluminum oxide) as a coating for ammonium perchlorate, omission of FeAA curing catalyst, and elimination of volatile contaminants from the binder. The importance of storing propellant in a dry environment and the effect of high temperature mechanical strength on cube fissuring behavior are shown.

¹Trademark of Cabot Corporation, Boston, Mass.

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Section I. (C) INTRODUCTION

(U) In the development of any propellant for service use, a major consideration is its thermal stability—a term which includes all types of chemical degradation influenced by temperature.¹ Because the decomposition of propellants may be manifested in many ways, such as the evolution of heat and gases and loss of weight, no single test exists for fully characterizing a given material. Deterioration of physical properties, development of internal fissures, loss of impulse, and spontaneous ignition result from such decomposition. The objective in the area of thermal stability is to develop propellants having a long useful shelf life over a wide range of service temperatures.

(C) This report summarizes the efforts of these Laboratories in evaluating and improving the thermal stability of high energy NF propellants based on NFPA² and TVOPA³. These propellants are made first by copolymerizing NFPA with a few percent of a second monomer containing a functionality suitable for later crosslinking. Several parts of TVOPA plasticizer are added to the copolymer to form the binder (normally 2:1 TVOPA:NFPA). The binder is mixed with solids (e.g., AP and Al) to form a relatively low solids-loaded (60 to 70%) propellant slurry. The slurry is cast and cured with a difunctional crosslinker added during mixing. Initial propellant had poor thermal stability which was manifested by the appearance of fissures caused by gaseous decomposition products. When the propellant was stored at the standard fissuring-test temperature (80°C), fissures appeared in 2-in. cubes in less than one day. This behavior, grossly unsatisfactory for Army world-wide service requirements, stimulated the thermal stability studies summarized in this report. Test methods which were used to evaluate the thermal stability problem are described as well as methods which led to its solution. Experimental results are included to demonstrate the significant improvements which were achieved. Fissuring times of about 500 hr in 2-in. cubes at 80°C can now be achieved routinely with RH-SE-103, a TVOPA/NFPA-AP-Al propellant selected for scale-up. This performance is deemed adequate for Army use [1].⁴ Although significant progress has been made, efforts to improve the thermal stability of this class of propellant are continuing.

¹Post cure and crystallization, which affect the storage stability of physical properties, are generally not considered in the province of thermal stability.

²NFPA: 2, 3-bis(difluoramino)propyl acrylate.

³TVOPA: 1,2, 3-tris[1, 2-bis(difluoramino)ethoxy]propane.

⁴Numbers in brackets refer to references at the end of the report.

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Preliminary tests of propellant made from a copolymer with improved control of molecular weight suggest that a significant improvement in fissuring time results from improved mechanical properties. Also, preliminary tests wherein the currently used vicinal form of NFPA is replaced by its geminal counterpart⁵ show improved thermal stability.

(U) Study of the thermal stability of propellants based on NFPA and TVOPA and of propellant ingredients has continued simultaneously with a research program for seeking improved formulations and a development program for scaling up the production of raw materials. Early in the program, the availability of propellant and propellant ingredients was very limited, and test methods were chosen which were applicable to small quantities of propellant. Vacuum gas evolution, differential thermal analysis, and small-scale fissuring tests (discussed below) were satisfactory for reflecting gross changes in thermal stability, but these tests were often insensitive to small changes in important constituents. These tests, therefore, were used primarily for screening purposes. An adiabatic calorimeter for determining the rate of thermal decomposition as a function of temperature was developed and used effectively in the study of propellants and propellant ingredients. Small changes in purity and small amounts of additives affected significantly the adiabatic decomposition rate, and, hence, the adiabatic heating rate became an important parameter for comparing the thermal stability of propellants and ingredients. As larger quantities of propellant became available, fissuring tests using 2-in. cubes of propellant were used extensively to verify thermal stability postulated from the small-scale tests. In general, qualitative agreement exists between the results of the small-scale tests and the larger-scale fissuring tests employing propellant cubes.

(U) The organization of topics discussed in this report is essentially chronological. Occasionally, however, several topics related to thermal stability were explored simultaneously, and the discussion of these topics is presented in the order which seemed most appropriate.

⁵Geminal NFPA: 2, 2-bis(difluoramino)propyl acrylate.

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Section II. (U) TEST METHODS

The primary methods used to evaluate the thermal stability of propellants and propellant ingredients in this study were vacuum gas evolution, differential thermal analysis, small-scale fissuring, adiabatic decomposition, and cube fissuring tests.

In the vacuum gas evolution test, a tube of known volume which contains the sample is first evacuated (Figure 1). The tube is then sealed by a valve in the top of the tube and placed in an isothermal oven. Periodically, the tube containing the sample is removed from the oven and attached to a vacuum manifold. A segment of the manifold which is adjacent to the sample tube and contains a pressure transducer has a known volume. After the manifold (including the segment of known volume) has been evacuated completely, a valve between the vacuum manifold and the calibrated segment is closed. The valve in the top of the sample tube is opened, and the evolved gases enter the segment of the manifold containing the pressure transducer. After the resulting pressure is recorded, the volume of gases evolved may be determined using perfect gas relationships. This data may be used for comparing the thermal stability of propellants and ingredients.

In the differential thermal analysis (DTA) test, a sample and a reference specimen—both approximately 10 mg—are placed in an oven and heated so as to produce a linearly increasing reference specimen temperature. An X-Y recorder is used to plot the difference between the sample and reference temperatures against oven temperature. Since an exotherm of the sample produces a peak on the record, the temperatures of the start and peak of the exotherm are established. In general, for the same heating rate, higher temperatures for the start of the exotherm correspond to the more stable samples. However, since small changes in ingredients often were not reflected by a change in the DTA record, differential thermal analysis was used only to denote gross differences in thermal stability.

Small-scale fissuring tests are conducted using about a 15-g sample of propellant case-bonded to a thin-wall, aluminum, test-tube capsule. The sample is placed in an isothermal oven at 70° or 80°C and removed periodically to be X-rayed. The time for internal fissures to develop or for a separation of the propellant from the capsule wall (case-bond failure) to occur is recorded. For propellants which do not shrink appreciably during cure, small-scale fissuring tests conducted at a temperature near the propellant

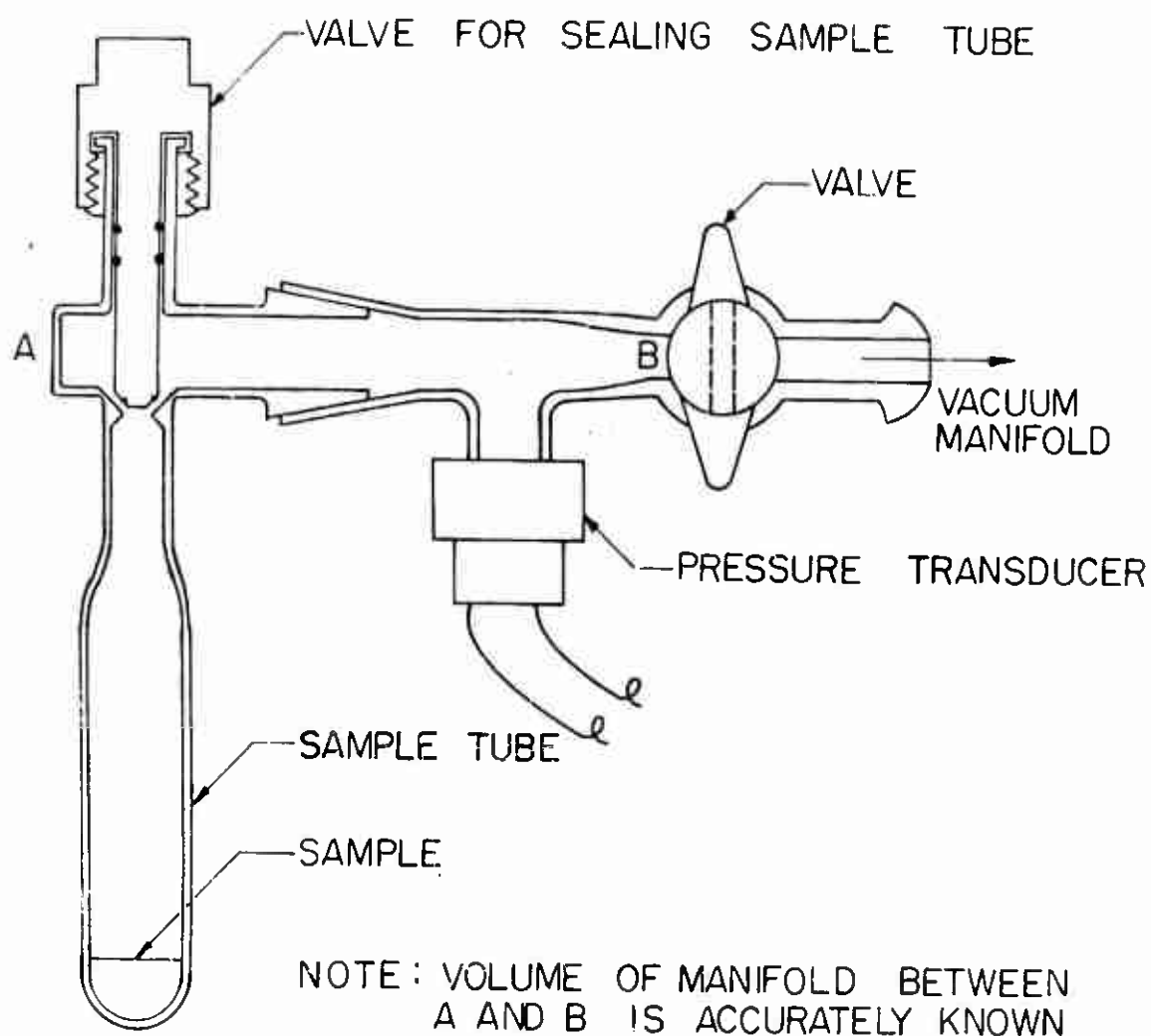


FIGURE 1. (U) GAS EVOLUTION APPARATUS

curing temperature do not case-bond fail and provide useful qualitative information about propellant thermal stability.

The adiabatic decomposition test provided the most significant quantitative information of any small-scale test used in the thermal stability evaluation of propellants and propellant ingredients. In this test, which is used to determine the adiabatic heating rate as a function of temperature, small changes in purity or additives cause distinct changes in the heating rate. A 15- to 25-g sample in a thin-wall, aluminum, test-tube capsule is placed in the center of a cylindrical adiabatic oven. A schematic of the adiabatic calorimeter is shown in Figure 2. A differential thermocouple between the capsule wall and oven wall supplies a signal to the oven power control system. The control system adjusts the power supplied to the oven heater to minimize the difference signal. A thermocouple in the center of the sample is used to record the temperature history during a test. A detailed description of the adiabatic calorimeter has been published [2].

Cube fissuring tests are conducted by wrapping (but not sealing) 2-in. cubes of propellant in aluminum foil, placing the cubes in an isothermal oven, and removing them periodically for X-ray. Since fissures are sometimes so oriented that detection from a single X-ray photograph is questionable, the propellant cubes are X-rayed from two directions 90° apart. When fissures are detected (or suspected) from the X-ray photographs, the cubes are sliced and inspected to confirm the failure. Several times an apparently sound cube (according to X-rays) has been sliced to insure that fissures were not being overlooked by the X-ray technique.

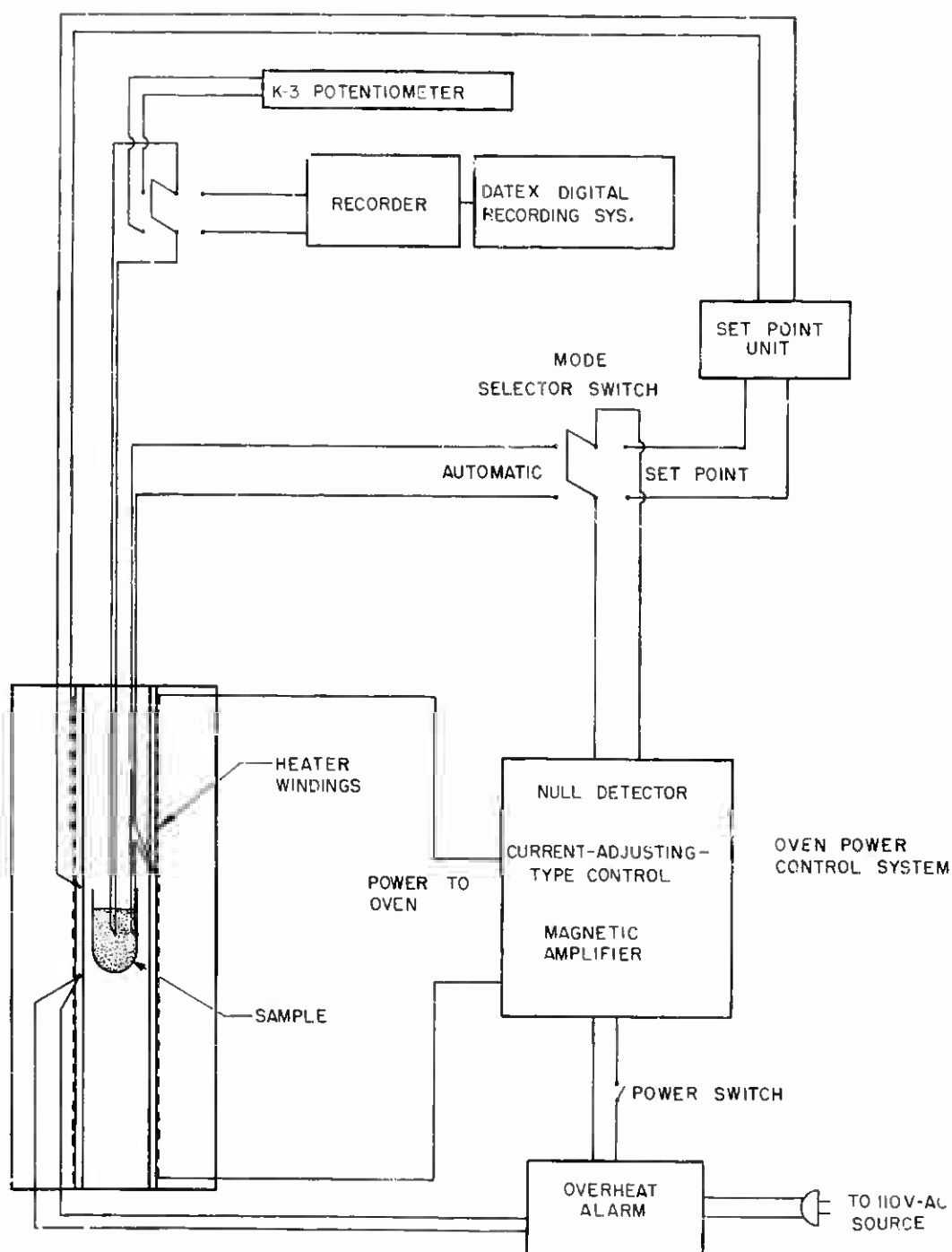


FIGURE 2. (U) ADIABATIC CALORIMETER SCHEMATIC

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Section III. (C) A PRELIMINARY EVALUATION OF SOME HIGH ENERGY PROPELLANTS (U)

(C) In the beginning of the development program for TVOPA/NFPA-AP-Al-type propellant, parallel efforts were expended in a preliminary evaluation of monomer-based RH-SA-103 propellant and prepolymer-based RH-SB-103 propellant. The monomer-based propellant was prepared by blending the ingredients (Table I) in a mixer with polymerization of the NFPA occurring after the slurry was cast into molds. In making RH-SB-type propellant, a copolymer of NFPA-hydroxypropyl methacrylate (HPMA) was first prepared, and hexamethylene diisocyanate (HMDI) crosslinker was added during the propellant mixing operation.

(C) During most of the evaluation program for these two propellant systems, only small quantities of propellant were available. Numerous adiabatic decomposition tests were performed using RH-SA-103 and RH-SB-103 propellant and, for comparison, plastisol-nitrocellulose propellant designated RH-P-112 (Table I). Representative temperature histories during adiabatic decomposition of these high energy propellants are shown in Figure 3.

Table I. (C) Propellant Compositions					
RH-P-112	Weight Percent	RH-SA-103	Weight Percent	RH-SB-103	Weight Percent
Ball Powder	16.7	NFPA(mon.)	13.0	NFPA (poly.) ¹	13.0
TEGDN	37.3	TVOPA	26.0	TVOPA	26.0
AP	30.0	AP	46.0	AP	46.0
Aluminum	15.0	Aluminum	15.0	Aluminum	15.0
Stabilizer	1.0				
¹ NFPA prepolymer contains up to 10% HPMA copolymer for cross-linking with HMDI. The crosslinker used in the propellant was in addition to the ingredients shown.					

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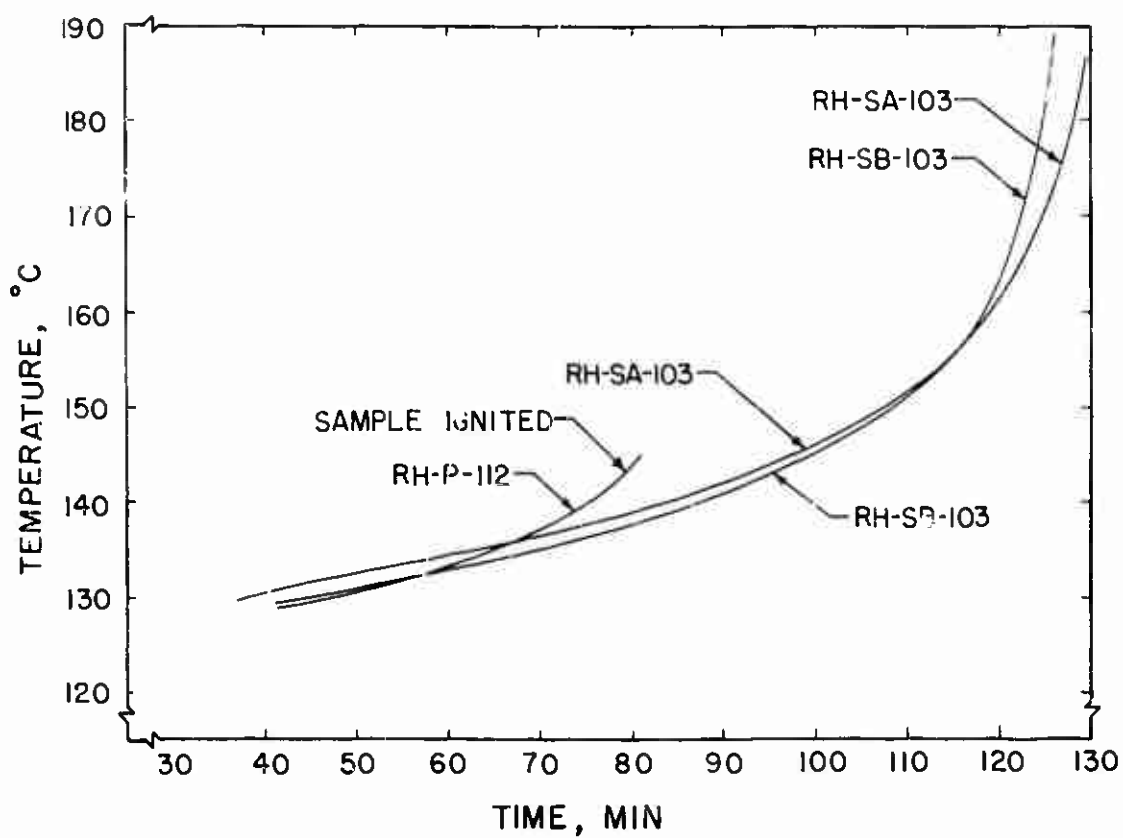


FIGURE 3. (U) TYPICAL TEMPERATURE HISTORIES DURING
ADIABATIC DECOMPOSITION

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(U) Since the rate of decomposition is associated with the propellant shelf life, a convenient and useful comparison of propellant thermal stability can be made on the basis of the adiabatic heating rate as a function of temperature. An enthalpy balance for a simple, zero-order reaction under adiabatic conditions gives

$$\sum(M_i C_i) \frac{dT}{dt} = M_p QZ \exp(-E/RT) \quad (1)$$

in which M_i represents the masses of individual materials which are heated by the decomposition reaction; C_i represents the corresponding specific heats; M_p is the mass of propellant; T is the temperature; t represents time; Q is the heat of decomposition; Z is the frequency factor; E is the activation energy; and R is the universal gas constant. During a typical adiabatic decomposition test, the fraction of sample decomposed (about 1%) is so small that the zero-order assumption does not invalidate the computations for the kinetic parameters. Dividing Equation 1 by M_p and taking the natural logarithm of both sides gives

$$\ln \left[\frac{\sum(M_i C_i)}{M_p} \frac{dT}{dt} \right] = \ln(QZ) - \frac{E}{RT} \quad (2)$$

from which it follows that a plot of $\ln \left[\frac{\sum(M_i C_i)}{M_p} \frac{dT}{dt} \right]$ against reciprocal temperature should give a straight line having slope $(-E/R)$ and intercept $\ln(QZ)$.

(U) A computer program was prepared to determine heating rates during decomposition using the recorded temperature history. The total temperature rise was divided into several uniform increments, and the rate of temperature rise at each nodal point between two increments was determined by differentiation of a second-degree polynomial fitted by the method of least squares to at least eight of the most adjacent time-temperature data points. The rate of temperature rise and reciprocal absolute temperature for each nodal point was substituted in Equation 2, and the method of least squares was used to determine E and the product QZ .

(U) Rate data from adiabatic decomposition tests using RH-SA-103, RH-SB-103, and RH-P-112 propellants could be described

quite well by the simple mathematical model of Equation 2. Kinetic parameters evaluated for several tests involving these propellants are presented in Table II. Typical within-batch reproducibility and batch-to-batch variations in the adiabatic heating rates for RH-SA-103 and RH-SB-103 propellants containing different lots of raw materials are shown in Figures 4 and 5, respectively. Batch-to-batch variations in the adiabatic heating rate for propellants containing the same lots of raw materials were insignificant, as shown in Figure 6. The most significant factor contributing to batch-to-batch variations in the adiabatic heating rate of NF propellants was differences in TVOPA purity, a fact which had not been established at the time these tests were conducted.

Table II. (U) Kinetic Parameters for Propellants

Propellant	E (kcal/mol)	QZ (cal/g-sec)	Heating Rate at 143°C ¹ (cal/g-sec)
RH-P-112 (batch 1800)	33.3	0.148×10^{16}	4.63×10^{-5}
	32.6	0.065×10^{16}	4.74×10^{-3}
	35.6	2.428×10^{16}	4.69×10^{-3}
	34.2	0.425×10^{16}	4.47×10^{-3}
	34.3	0.527×10^{16}	4.91×10^{-3}
RH-SA-103 (batch 1061)	26.1	4.067×10^{10}	7.75×10^{-4}
	26.6	6.865×10^{10}	7.14×10^{-4}
	26.3	4.947×10^{10}	7.40×10^{-4}
	24.6	0.720×10^{10}	8.43×10^{-4}
RH-SB-103 (batch 665)	25.4	0.069×10^{12}	3.07×10^{-3}
	27.5	0.781×10^{12}	2.73×10^{-3}
	25.9	0.116×10^{12}	2.82×10^{-3}
	27.9	1.294×10^{12}	2.70×10^{-3}
¹ The heating rate is tabulated at 143°C since this temperature is about midway between the initial and final temperatures for the tests.			

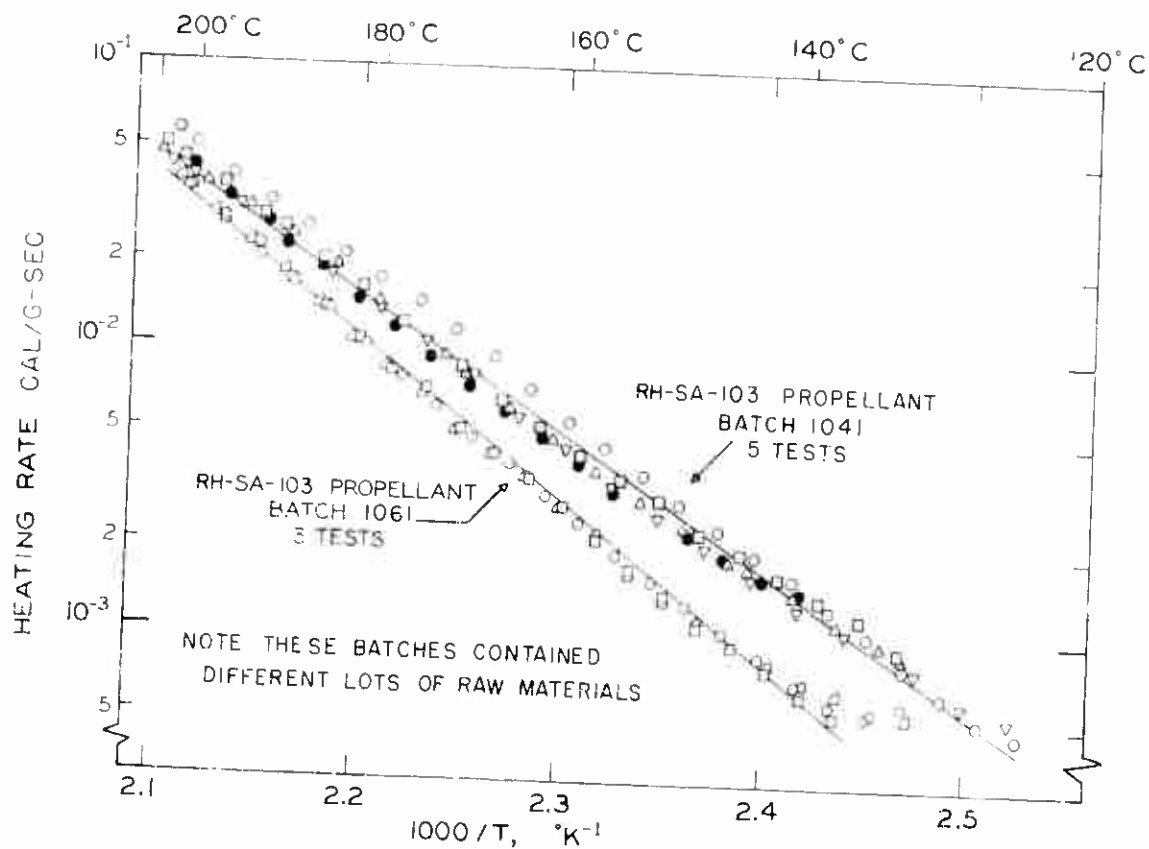


FIGURE 4. (U) ADIABATIC DECOMPOSITION TEST REPRODUCIBILITY
FOR RH-SA-103 PROPELLANT

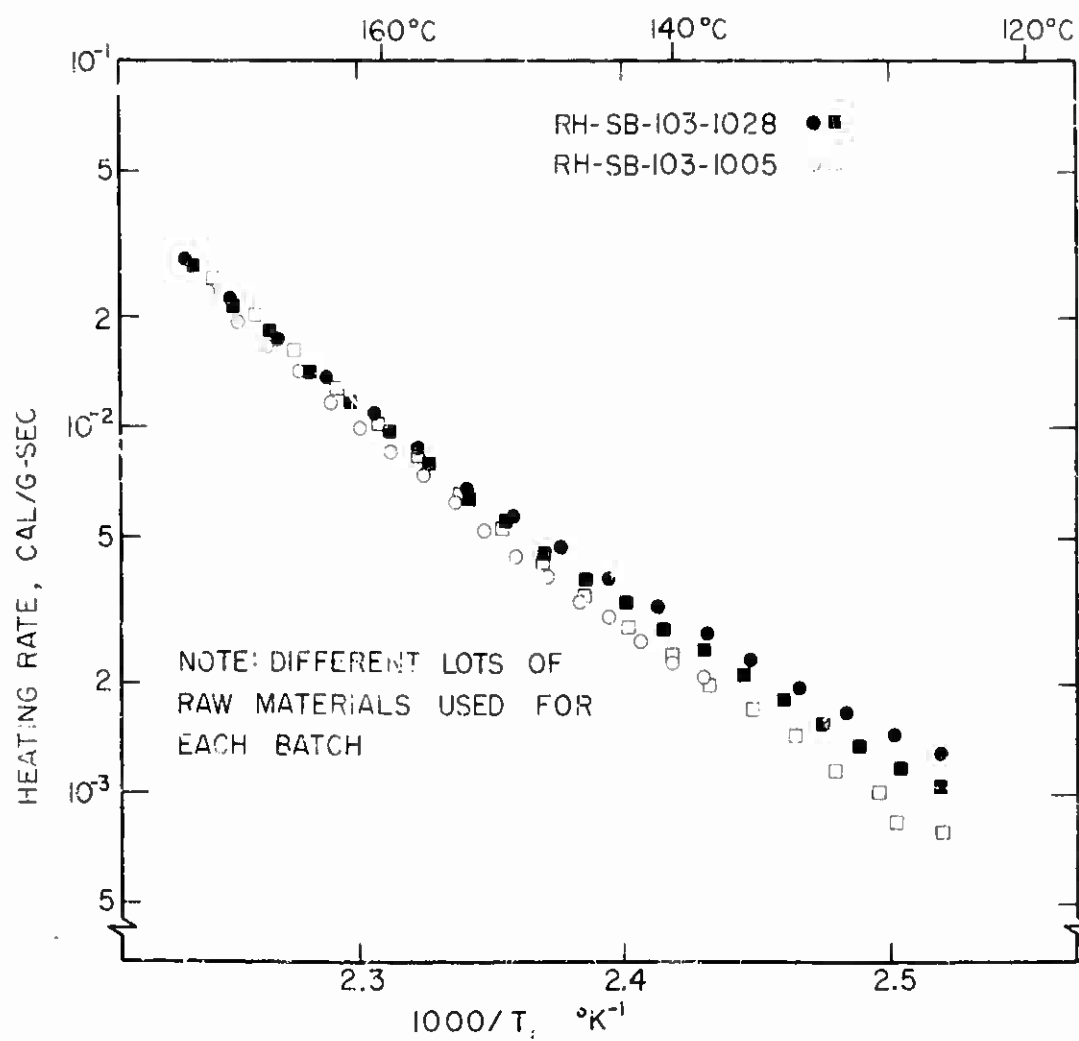


FIGURE 5. (U) ADIABATIC DECOMPOSITION TEST REPRODUCIBILITY
FOR RH-SB-103 PROPELLANT

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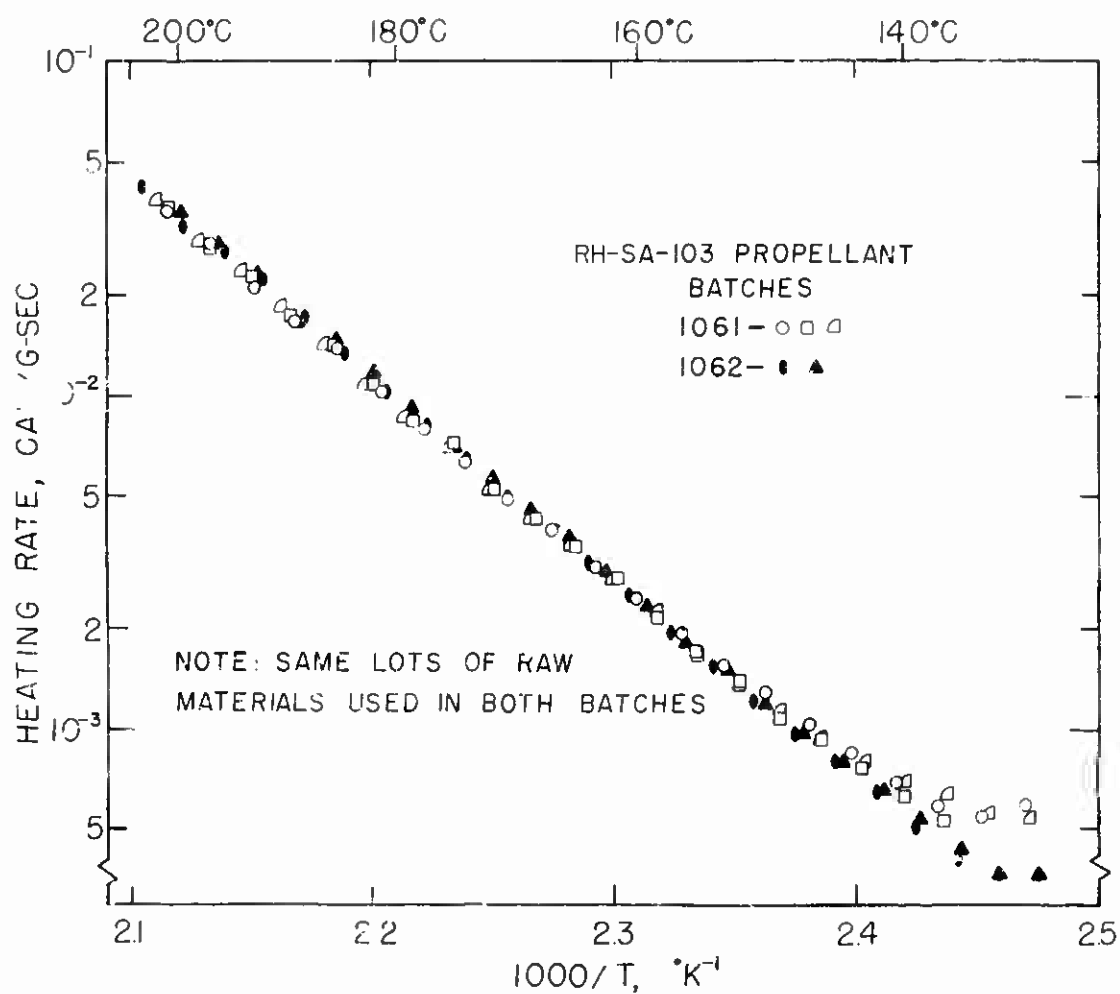


FIGURE 6. (U) ADIABATIC DECOMPOSITION TEST REPRODUCIBILITY

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(C) Figure 7 shows representative adiabatic heating rates for RH-SA-103, RH-SB-103, and plastisol RH-P-112 propellants as well as a later NF formulation, RH-SE-103. While the rate of decomposition for RH-SB-103 propellant was in the same range as the rate for plastisol at 120°C, the rate of decomposition for plastisol increased much more rapidly with increasing temperature than that of the RH-SA-103 and RH-SB-103 propellants. Extrapolation of these results to lower temperatures indicated that RH-P-112 propellant might be expected to give better thermal stability behavior than RH-SA-103 or RH-SB-103 at normal service temperatures. Vacuum gas evolution and small-scale fissuring test results at 80°C supported this conjecture (Table III).

Table III. (C) Gas Evolution and Fissuring Results (U)		
	Gas Evolved After 120 hr at 80°C (cc STP/g)	Time to Fissure at 80°C (hr)
RH-P-112	0.26	200
RH-SA-103	0.31	150
RH-SB-103	0.47	30

(U) From the standpoint of thermal stability, the data presented above clearly demonstrate the superiority of monomer-based RH-SA-103 over the prepolymer-based RH-SB-103 propellant; however, problems associated with shrinkage and 18-kcal/mol exotherm which accompany the polymerization of NFPA favored the development of prepolymer-based propellant, and development of monomer-based propellant was discontinued.

(C) The difference in the stability of RH-SA-103 and RH-SB-103 propellants was ascribed to the HPMA-HMDI crosslinking system used in the RH-SB-103 propellant, and a series of adiabatic decomposition tests was conducted to investigate this hypothesis. For this series of tests, several batches of RH-SB-103 propellant were prepared using the same lots of raw materials with the samples differing only in the HMDI crosslinker level. The experimental data shown in Figure 8 revealed that a reduction in the HMDI crosslinker level (indicated by the NCO/OH equivalence ratio in Figure 8) resulted in a decrease in the adiabatic heating rate. These tests verified the close

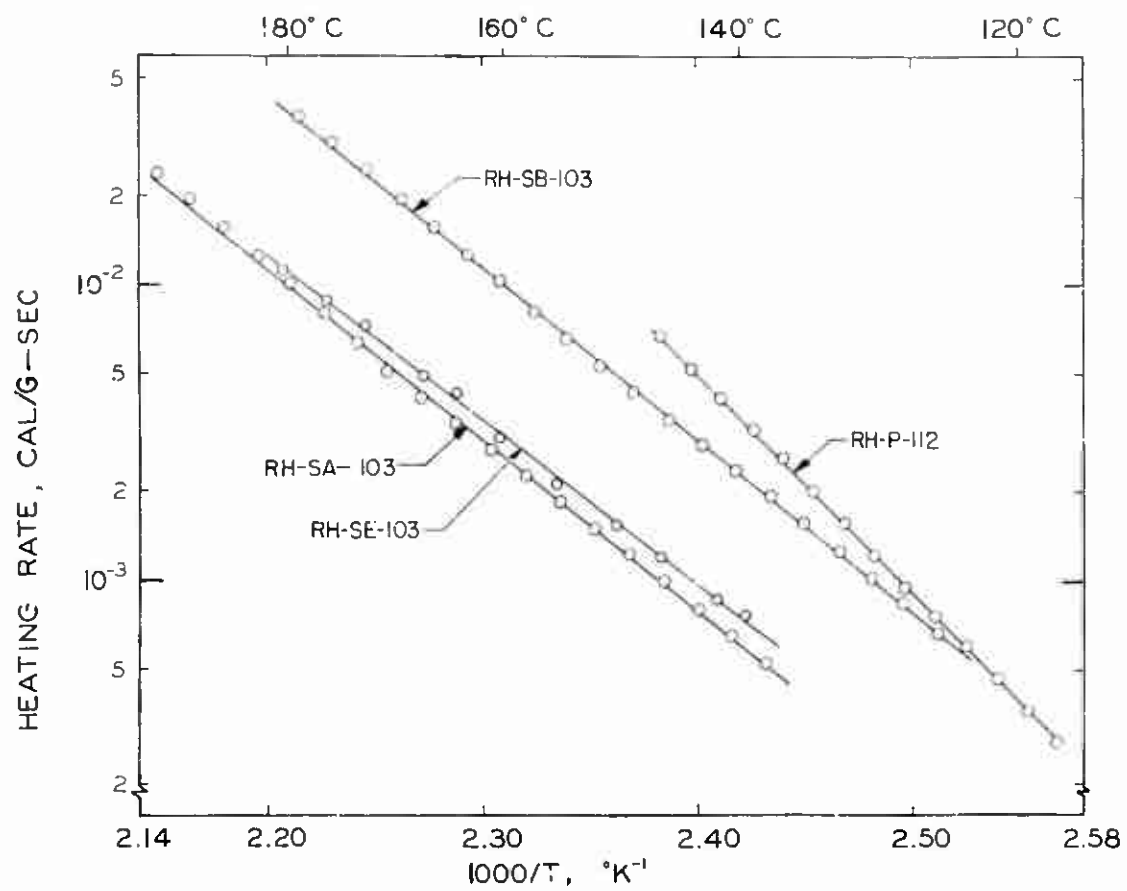


FIGURE 7. (U) COMPARISON OF ADIABATIC DECOMPOSITION RATES

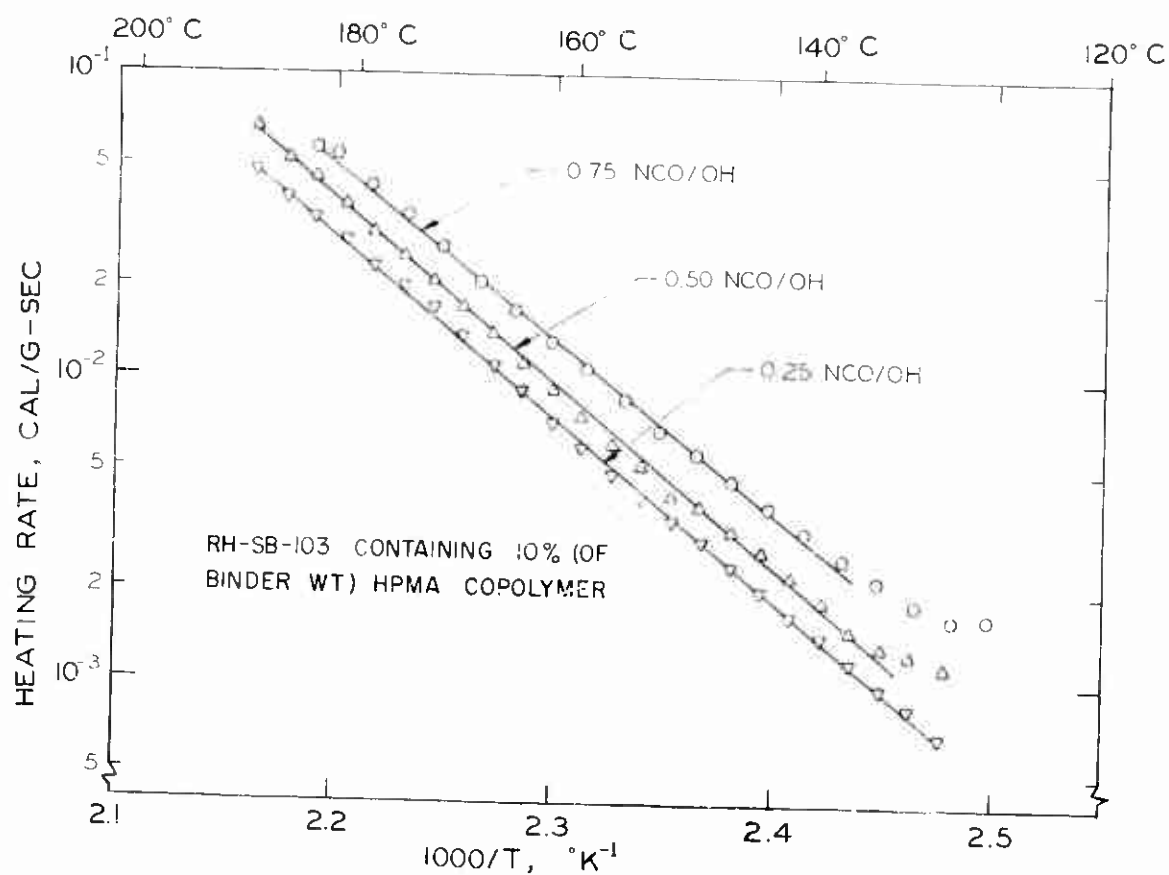


FIGURE 8. (U) EFFECT OF CROSSLINKER CONCENTRATION ON ADIABATIC DECOMPOSITION

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relationship of the crosslinker level with the thermal stability problem in RH-SB-type propellant, and a more stable crosslinking system was sought for prepolymer-based propellant. Furthermore, the data in Figure 8 demonstrated the utility of the adiabatic calorimeter for determining the effect of small compositional differences on thermal stability behavior of propellant.

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Section IV. (C) SEARCH FOR STABILIZING ADDITIVES (U)

(C) During the search for an improved crosslinking system, prospective stabilizing ingredients were screened. Small batches of RH-SB-103 binder containing 10% by weight HPMA and 0.5 equivalents of NCO/OH were mixed with 2% by weight of the stabilizer, were cast into small glass test tubes and sealed with corks, and were cured overnight in a water bath at 50°C. The bath temperature was then raised to 80°C and the samples were observed over a 45-hr period. The results are summarized in Table IV.

Table IV. (C) Stabilizer Screening Results with RH-SB-103 Propellant (U)	
Additive	Comments
None (control)	fissured in 26-44 hr
Norit-A ^{®1} (carbon black)	voids in 18 hr
Alon-C ^{®2} (Al ₂ O ₃)	appeared good after 45 hr
Linde Molecular Sieve MS-4A	fissured in 26-44 hr
Linde Molecular Sieve MS-5A	fissured in 26-44 hr
Benzoyl fluoride	fissured in 18 hr
Resorcinol	voids in 18 hr
Boric oxide	possible voids, but little gassing at 44 hr
Sodium fluoride	much gassing after 42 hr
Tetraethyl orthosilicate	much gassing after 42 hr
Cab-O-Sil ^{®3}	very little gassing after 42 hr
¹ Trademark of Fisher Scientific Company, Pittsburgh, Pa. ² Trademark of Cabot Corporation, Boston, Mass. <u>Note:</u> Alon-C is no longer available from Cabot Corporation; however, the same material is available from Degussa Inc., Pigments Division, Schuyler Avenue, Kearny, New Jersey. ³ Trademark of Cabot Corporation, Boston, Mass.	

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(C) The results from the screening tests indicated that Cab-O-Sil, Alon-C, and boric oxide might be suitable stabilizers for NF propellants. To determine the effect of these additives on the time to fissure in the small-scale fissuring test, small batches of RH-SB-103 propellant which contained 1% by weight (based on binder) of these ingredients were prepared, using the same lots of raw materials. Another batch of RH-SB-103 propellant was prepared which had the usual 1% tricalcium phosphate (TCP) coating (based on AP) on the ammonium perchlorate (AP) replaced with 1% Cab-O-Sil (based on AP) and which contained 1% Cab-O-Sil by weight (based on binder) dispersed in the binder. A control batch of RH-SB-103 propellant containing no stabilizer was also prepared to give a basis for comparison. Aluminum test-tube capsules lined with Paraplex[®] P-43 resin served as sample containers. From the results (Table V), Cab-O-Sil and Alon-C appeared to be the most promising candidates.

Table V. (C) Small-Scale Fissuring Data for Stabilizer Screening in RH-SB-103 Propellant (U)		
Stabilizer	Temperature	Comments
None (control)	60°C	Fissured 55-73 hr
1% Cab-O-Sil	60°C	Case-bond failure 73-79 hr
1% Alon-C	60°C	Case-bond failure 73-70 hr
None (control)	70°C	Several small fissures 7-24 hr
1% Cab-O-Sil	70°C	Case-bond failure 48-55 hr
1% Alon-C	70°C	Fissured 79-144 hr
1% Boric oxide	70°C	Fissured 73-79 hr
1% Cab-O-Sil on AP + 1% in binder	70°C	Fissured 79-144 hr

⁶Trademark of Rohm and Haas Company, Philadelphia, Pa.

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(C) Larger batches of monomer-based RH-SA-103 propellant were prepared from the same blends of raw materials to observe the effect of Cab-O-Sil and Alon-C on the time-to-fissure for 2-in. cubes. A control batch containing no stabilizer was also prepared for comparison. Several cubes from each batch were tested at 70°C and 80°C and representative data are presented in Table VI. As in the small-scale fissuring test, 2-in. cubes containing either Cab-O-Sil or Alon-C demonstrated longer fissure-times than the control batch. To this point in the development program, TCP had been the standard coating for AP. However, since Alon-C gives better thermal stability and also serves as an anti-caking agent, TCP was replaced by Alon-C as the standard coating for AP used in NF propellant.

Table VI. (C) 2-in.-Cube Fissuring Results for RH-SA-103 Propellant with Various Stabilizers (U)			
Batch	Stabilizer	Hours to Fissure	
		70°C	80°C
1082	None (control)	72-80	7-24
1083	Cab-O-Sil	545-570	30-45
1084	Alon-C	No Data	55-75

(C) Later in the propellant development program, an investigation was conducted to determine the effect of various oxidizer coatings on the thermal stability of RH-SE-103 propellant, a formulation similar to RH-SB-103 which was later selected for scale-up.⁷ Eight coatings were investigated along with uncoated oxidizer. Table VII lists the oxidizer coatings and the corresponding RH-SE-103 propellant batch numbers. All batches were processed using the same lots of raw materials. The differences between RH-SE-103 and RH-SB-103 (Table I) propellants existed completely within the binder system; the weight percentages of AP and Al were the same for both propellants. The binder for RH-SE-103 propellant contained 2/1 TVOPA/ copolymer (b, weight) and the copolymer was synthesized with 94% NFPA and 6% acrylic acid. Curing was accomplished through a di-epoxide curing agent. The uncoated ammonium perchlorate had a

⁷Other factors related to the thermal stability of RH-SE-103 propellant are discussed in Section VII.

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nominal particle size of 43μ . The epoxide/acrylic acid equivalency ratio was 1.5/1 for all batches. The AP was coated by combining 1% by weight of the test material with the oxidizer and mixing in a rotary blender for 30 minutes. One test material, the potassium aluminum oxalate, caused agglomeration of the AP and had to be added directly to the propellant slurry when Batch 34 was made. The three thermal stability tests employed in this evaluation were DTA, vacuum gas evolution, and small-scale propellant fissuring tests, and the purpose of the tests was to ascertain gross differences in stability.

Table VII. (U) Oxidizer Coatings for RH-SE-103 Propellant	
Batch No.	Oxidizer Coating
24	Tricalcium phosphate (TCP)
25	None
26	Magnesium oxide (MgO)
28	Cab-O-Sil (SiO_2)
30	Alon-C (Al_2O_3)
32	Aluminum acetylacetonate [$\text{Al}(\text{AA})_3$]
33	Thorium acetylacetonate [$\text{Th}(\text{AA})_3$]
34	Potassium aluminum oxalate [$\text{K}_3\text{Al}(\text{C}_2\text{O}_4)_3$]
35	Aluminum basic acetate (AlOOAc)

(C) Three types of samples were prepared for differential thermal analysis: (1) coated AP, (2) coated AP/TV O in a 50/50 mixture, and (3) the cured RH-SE-103 propellant. Duplicate runs were made with most of the DTA samples. Examination of the data (Table VIII) showed no gross differences among the samples with a single type. For example, the propellants which are of primary interest all fall within a 10° spread (225° to 235°C). Similarly, the oxidizer/TVOPA samples lie in a common range (254° to 267°C). More spread is noted in the dry, coated AP (about 50°), but the significance of shifting of the first peak in the decomposition has not been determined.

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Table VIII. (C) DTA Data for Oxidizer Coating Study (U)			
Coating	Peak Exotherm Temperatures, C°		
	Coated AP ^a	Coated AP/TVOPA ^b	RH-SE-103 Propellant with Coated AP
TCP	301	261	225
	312	262*	226
None	330	261*	234
	321	258*	229
MgO	341	259*	225
	352	268*	229
Cab-O-Sil	310	254*	229
	310		228
Alon-C	324	262	229
	330		235
Al(AA) ₃	316	260	229
	316	255*	233
Th(AA) ₃	312	258	222
	330		228
K ₃ Al(C ₂ O ₄) ₃	336	265	228
	320		231
AlOOAc	312	267	232
	330	267	234
^a Exotherm preceding primary decomposition ^b 50/50 Mixture * Sample exploded			

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(C) Vacuum gas evolution tests were conducted on a single sample of each of the cured propellants. Pressure measurements were made on the samples after selected intervals of heating at 80°C. Evacuation of the tube containing the sample succeeded each pressure measurement. The amount of gas evolved as a function of time was obtained by assuming the individual pressures to be cumulative. As in the DTA tests, the gas evolution tests revealed no gross differences in thermal stability (Table IX). After heating for 25 hr. all samples had evolved 0.12 ± 0.05 cc of gas/g of propellant; and after 100 hours, 0.37 ± 0.09 cc/g. The batch containing MgO gave off the least amount of gas after 100 hours, while the batch containing uncoated oxidizer gave off the most for this period of time.

Table IX. (C) Gas Evolution Data for Oxidizer Coating Study for RH-SE-103 Propellant (U)				
Coating	Batch No.	Volume of Gas Evolved, cc/g STP		
		25 hrs at 80°C	50 hrs at 80°C	100 hrs at 80°C
TCP	24	0.14	0.20	0.33
None	25	0.18	0.27	0.46
MgO	26	0.07	0.14	0.28
Cab-O-Sil	28	0.11	0.18	0.37
Alon-C	30	0.12	0.17	0.31
Al(AA) ₃	32	0.08	0.15	0.30
TH(AA) ₃	33	0.11	0.21	0.41
K ₃ Al(C ₂ O ₄) ₃	34	0.11	0.16	0.29
AlOOAc	35	0.10	0.13	0.29

(C) Small-scale fissuring studies were conducted at 70°C and 80°C using approximately 15-g samples of case-bonded propellant in 3/4-in.-diameter aluminum test tubes. Case-bond failures, as well as fissures, terminated the test when they occurred. For each sample two times are shown in Table X which bracket the actual time-to-failure. The shorter time represents the last X-ray before fissuring, and the longer time represents the X-ray on which the failure was detected. The times-to-failure are higher than average for the samples containing Alon-C and AlOOAc and much lower for

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the samples containing $\text{Th}(\text{AA})_3$. Al, most of the samples failed between 250 and 350 hr. Although the samples containing Alon-C and aluminum basic acetate had longer times-to-failure than the majority of the samples, the scatter in the data for these two coatings made it difficult to assess the magnitude of improvement.

(C) Appraisal of the tests involving the eight AF coatings suggests that the DTA test is not of value in a problem of this nature. Apparently, differences in propellants with 1% or less changes in composition are difficult to detect by this method. Likewise, the gas evolution data, alone, seem to be of little value, since all of these propellants gave approximately the same volume of gas per unit time. If significance could be attached to the small differences in gas evolution data, the propellant containing MgO would be among the best. However, the propellant containing MgO was among the worst in time-to-fissure. Therefore, small differences in the gas evolution data should be discounted. The only useful information derived from this series of tests is the small-scale fissuring data. These fissuring data, while perhaps not quantitatively significant, did testify that Alon-C is a satisfactory coating for AP in RH-SE-103 propellant, and its use as a standard coating was continued.

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Table X. (C) Small-Scale Fissuring Data for Oxidizer Coating Study for RH-SE-10 ³ Propellant (U)			
Coating	Batch No.	Hours to Fissure at	
		70°C	80°C
TCP	24	247-264	103-168 24-89 95-161
None	25	264-271	103-168 24-89 96-161
MgO	26	223-240	103-168 24-89 89-154
Cab-O-Sil	28	336-353 328-336	24-89 120-137
Alon-C	30	492-564 761-785	210-216* 260-264*
Al(AA) ₃	32	324-395	89-113 89-113 89-96 113-120
TH(AA) ₃	33	0-65*	0-65 0-17 55-75
K ₃ Al (C ₂ O ₄) ₃	34	257-264 264-281 235-305	96-113 96-161 79-144
AlOOAc	35	336-360 624-744	168-233 199-216
*Case-bond failure			

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Section V. (C) THERMAL STABILITY OF TVOPA (U)

(U) After the utility of the adiabatic calorimeter for detecting the effect of small changes in constituents on thermal stability had been demonstrated for propellants, a program for defining the effect of impurities on the thermal stability of TVOPA was initiated.

(U) Preliminary adiabatic decomposition experiments were conducted using untreated TVOPA Batch 804 made at these Laboratories and TVOPA Batch 821 made by Aerojet-General Corporation. The production of Aerojet's TVOPA Batch 821 included a thermal soaking at 115°C, followed by distillation with removal of forerun and pot residue. Figure 9 clearly shows the superior thermal stability of Batch 821 over untreated TVOPA Batch 804. Figure 9 also shows that thermal soaking and distillation reduced the decomposition rate of Batch 804 TVOPA significantly. For simplicity, smooth curves were drawn to represent the heating rate for individual tests. In general, the adiabatic heating rate versus reciprocal absolute temperature could be represented on a similar plot by straight lines. This merely implies that the previously described model for the decomposition of propellants is not suitable for describing the decomposition of TVOPA.

(C) In an effort to establish factors affecting the thermal stability of TVOPA, adiabatic decomposition tests and infrared analyses were performed using several batches of TVOPA. Since the adiabatic heating rate curves for TVOPA were roughly parallel (Figure 9), a fair and hasty comparison of TVOPA stability could generally be obtained by observing the heating rate at 143°C ($1000/T^{\circ}K = 2.40$), about midway in the temperature range covered. Table XI summarizes the data from this series of tests. These results demonstrated that the adiabatic decomposition behavior of TVOPA was greatly improved by acid washing (Batch 804, tests 159 and 178; and Batch 832, tests 170 and 180) or by passing through an ion-exchange column containing Amberlyst[®] 15 resin (tests 159 and 183). Attempts were made to correlate the adiabatic decomposition rates with each of the seven infrared absorption bands. The 5.96 μ absorption correlated well with the adiabatic decomposition rate as shown in Figure 10; none of the other absorptions gave such striking correlations.

⁸ Trademark of Rohm and Haas Company, Philadelphia, Pa.

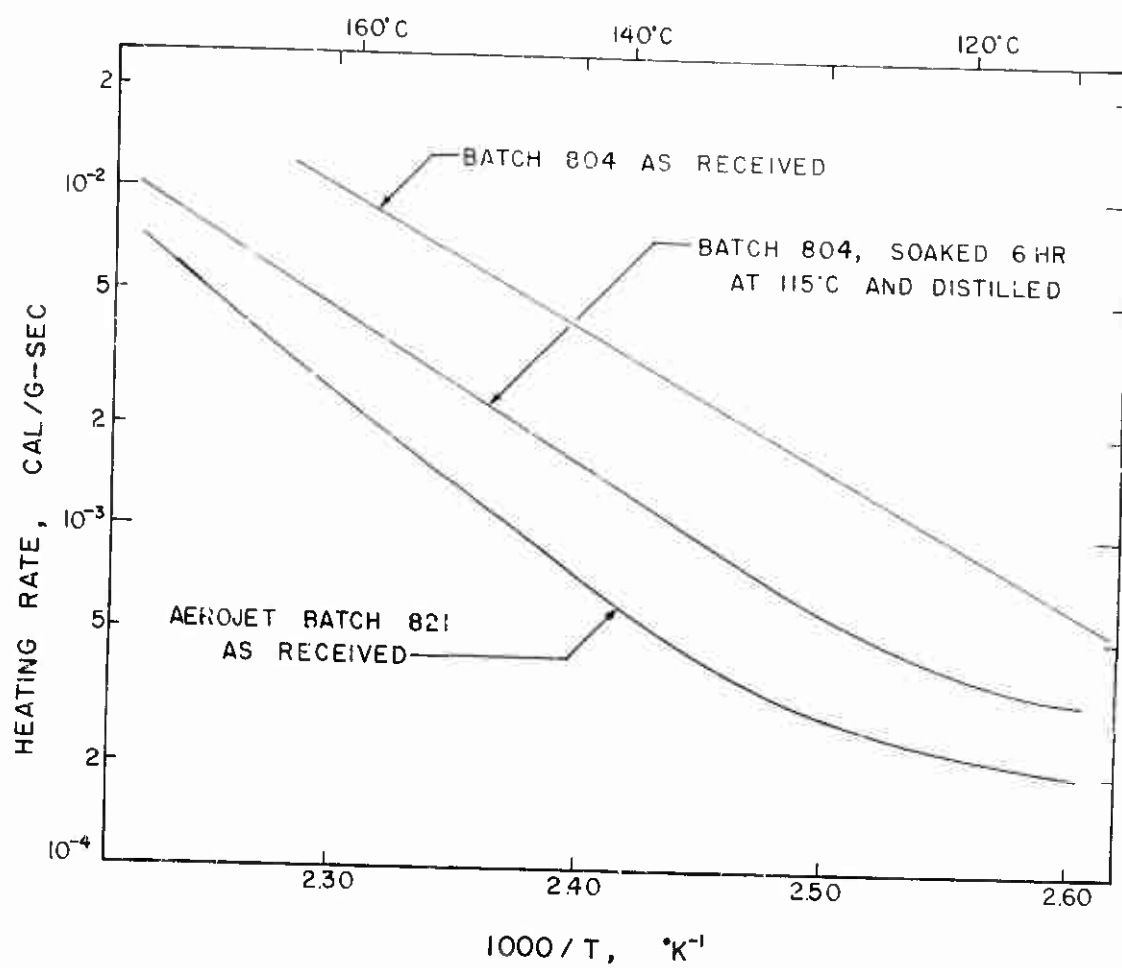


FIGURE 9. (U) ADIABATIC DECOMPOSITION OF TVOPA

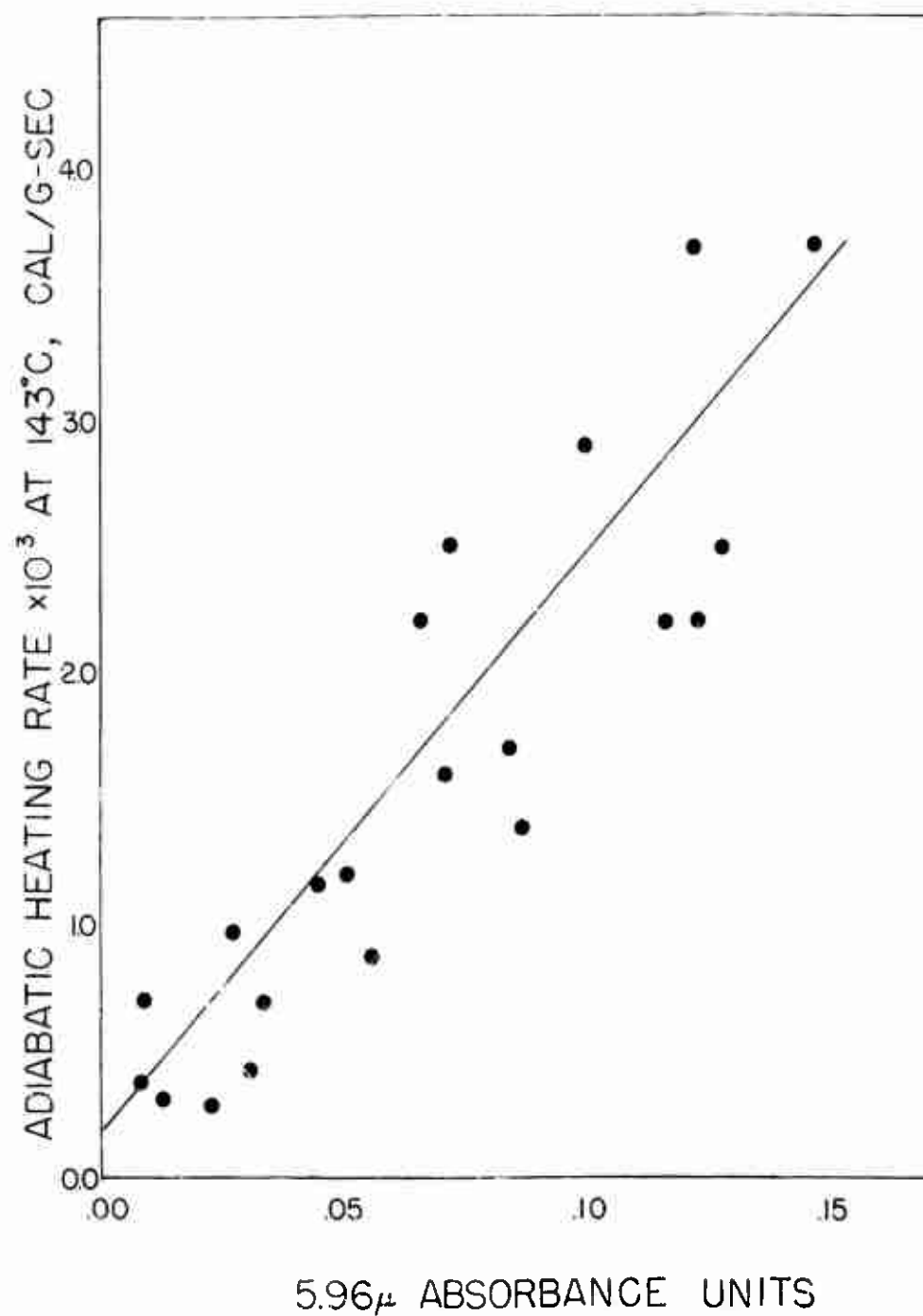


FIGURE 10. (U) ADIABATIC DECOMPOSITION CORRELATION FOR TVOPA

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Table XI. (C) Infrared and Adiabatic Decomposition Data (U)									
TVOPA Batch	Test No.	Infrared Spectrometer Analysis					Adiabatic Heating Rate at 143°C (cal/g-sec)		Comments
		OH (%)	C=C (%)	NONE (%)	5.78μ (AU)	5.96μ (AU)	6.23μ (%)	6.40μ AU	
804	159	0.20	0.25	-	0.035	0.147	0.28	-	untreated, production grade (test run June 1965)
804	177	0.40	-	-	0.025	0.190	0.18	-	untreated, production grade (test run August 1965)
804	162	0.14	-	-	0.008	0.066	0.34	-	2 hours at 110°C and fractionated
804	165	0.13	-	-	0.016	0.071	0.52	-	6 hours at 110°C and fractionated
804	178	trace	-	-	-	0.013	0.10	-	sulfuric acid washed
804	183	0.30	-	-	0.034	0.007	0.34	-	passed through column of Amberlyst 15
821	155	0.50	0.20	-	0.086	0.034	0.26	-	production-grade Aerojet TVOPA (cooled at 115°C and distilled)
832	180	0.85	-	2.55	0.190	0.123	0.32	trace	blend of out-of-spec material
832	170	0.04	-	-	0.001	0.023	0.19	-	Batch 832 after sulfuric acid wash
869-1	175	0.47	0.47	-	0.028	0.073	0.30	-	distilled TVOP

¹An explanation of the tabulated values for the infrared analyses is included in an appendix to this report.

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(C) In order to observe the effect of various impurities on the adiabatic heating rate of TVOPA, a portion of TVOPA Batch 869-1 was washed with sulfuric acid. Samples for adiabatic decomposition were prepared by salting individual portions of the acid-washed TVOPA with about 1% of the various impurities. Adiabatic heating rates at 143°C, gas evolution data, and infrared spectra for the samples are shown in Table XII. The following points are confirmed by the data in Table XII:

- (1) The sulfuric acid wash improved the adiabatic decomposition rate and gas evolution rate of production grade TVOPA Batch 869-1. Previous acid washing of Batch 804 resulted in a greater improvement in the adiabatic heating rate; however, Batch 869-1 before acid washing was better than the unwashed Batch 804.
- (2) Salting with OH, NONF, and the 6.23 μ fluorimino cyanide impurity produced relatively little effect for the amounts added in these tests.
- (3) Salting with 1% TVOP resulted in a pronounced increase in adiabatic heating rate.
- (4) Salting with water, acetaldehyde (CH₃CHO), or chloromethyl dioxolane gave little change (possible improvement) in decomposition behavior, indicating that for the quantities of the salted ingredients involved, hydrolysis and/or hydrolysis products did not have a pronounced adverse effect in these tests. It should be noted, however, that the tests started at a temperature above the boiling point of water, so it is questionable how much water remained within the sample during the test.
- (5) Salting with the 5.96 μ fluorimino carbonate impurity increased the adiabatic heating rate significantly.

(C) The previously described correlation of decomposition rate with the value of the 5.96 μ absorbance was substantiated in essence by this series of tests; however, the samples salted with TVOP (which contains double-bonded carbon atoms) were notable exceptions. Since a low value of the absorbance unit at 5.96 μ is a necessary, but not sufficient, condition for a low adiabatic heating rate, the 5.96 μ impurity is obviously not the complete key to TVOPA thermal stability.

Table XII. (C) Summary of TVOPA Salting Experiments with Batch 869-1 (U)

Sample Identification	Test	Infrared Spectrometer Analysis						Gas Evolved at 80°C in 150 hr (cc/g ± STP)	Adiabatic Heating Rate at 143°C (cal/g-sec)	Comments
		OH (%) ¹	C=C (%) ²	NONE (%) ³	5.78 μ (AU) ⁴	5.96 μ (AU) ⁴	6.23 μ (%) ⁵	6.40 μ (AU) ⁶		
865-1	186	0.50	-	0.90	0.095	0.084	0.21	0.020	1.7×10^{-3}	Production grade washed with sulfuric acid
865-1 acid washed	188	trace	-	0.15	0.019	0.027	0.13	-	0.97×10^{-3}	
salied ¹ -6.23 μ	190	trace	-	0.40	0.045	0.045	0.89	-	1.16×10^{-3}	mixed alcohols added analysis questionable ²
salied ¹ -OH	191	0.65	-	0.87	0.075	0.051	0.21	-	1.2×10^{-3}	
salied ¹ -TVOP	193	0.35	-	-	0.231	0.038	trace	-	4.22×10^{-3}	5.7 μ interfered with 5.76 μ 4 chloromethyl dioxolane
salied ¹ -CH ₃ CHO	199	trace	-	0.70	0.143	0.078	0.26	-	0.89×10^{-3}	
salied ¹ -CMDO	202	trace	-	-	0.030	0.051	0.16	-	0.60×10^{-3}	3 drops in 15 g TVOPA
salied ¹ -5.96 μ	206	0.42	-	0.50	0.090	0.324	0.23	-	4.6×10^{-3}	
salied ¹ -H ₂ O	207	0.33	-	trace	0.028	0.048	0.17	-	0.42×10^{-3}	
salied ¹ -NONE	214	0.37	-	1.83	0.078	0.958	0.29	-	0.61×10^{-3}	
salied ¹ -TVOP ³	210	trace	0.99	trace	0.151	0.054	0.18	-	8.24×10^{-3}	

¹Inpurities were always added to sulfuric acid washed TVOPA 869-1.

²TVOP was mixed with TVOPA before stripping. Analysis was delayed and may not correspond to test sample.

³TVOP was mixed with neat TVOPA. Possibility of poor mixing. Analysis changed with time.

⁴C=C indicates double-bonded carbon atoms.

⁵Weight percent obtained from infrared spectrometer analysis. See appendix for further explanation.

⁶Absorbance units by infrared spectrometer. See appendix for further explanation.

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(C) Test results from additional adiabatic decomposition experiments which were conducted to observe the effect of various treatments and additives on the adiabatic heating rate of TVOPA are summarized in Table XIII. Samples for all the tabulated tests were prepared from TVOPA Batch 134. Tests were performed using the production-grade TVOPA which had been passed three times through a column of Amberlyst-15, and TVOPA which had been passed three times through a column of Amberlyst and salted with small quantities of TVOP and ferric acetylacetonate (FeAA). The effect of FeAA on thermal stability of TVOPA was sought since FeAA was used to some extent as a curing catalyst for NF propellants. The table clearly shows the significant improvement in the heating rate which followed the ion-exchange treatment. Furthermore, the results indicate that either 0.5% TVOP or less than 1% FeAA is sufficient to increase the adiabatic heating rate significantly. The presence of about 1% acetyl chloride in TVOPA produced no significant change in the heating rate (test 336).

Table XIII. (C) Adiabatic Decomposition Studies of TVOPA (Batch 134) (U)		
Test	Adiabatic Heating Rate at 143°C (cal/g-sec)	Treatment/Comments
332	4.2×10^{-3}	Production-grade Batch 134
331	0.54×10^{-3}	Three passes Amberlyst column
334	8.0×10^{-3}	Three passes Amb. column; 0.5% TVOP by weight added before testing
336	0.6×10^{-3}	Three passes Amb. column; acetyl chloride (about 1% by weight) added before testing
338	2.7×10^{-3}	Three passes Amb. column; 0.88% FeAA by weight added before testing
342	0.58×10^{-3}	Three passes Amb. column; 0.15 % FeAA by weight added

(C) A series of tests was conducted to compare the decomposition behavior of TVOPA subjected to an ion-exchange treatment using Amberlyst-15 with that of TVOPA subjected to sulfuric acid washing using TVOPA blend 100. In addition, the effect of removing the

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alcohol impurity by an Amberlyst-15 catalyzed reaction with acetic anhydride or acetyl chloride was investigated. The adiabatic heating rates at 143°C are shown in Table XIV for tests in this series. Comparison of the heating rates for tests 349 and 351 with the rates for tests 353 and 355 indicates that the Amberlyst-15 treatment resulted in an improvement in adiabatic heating rate equally as good as the sulfuric acid wash. The tabulated heating rates for tests 359, 361, 364, and 366 indicate that no additional improvement in adiabatic heating rate followed the removal of the alcohol impurity by an Amberlyst-15 catalyzed reaction with acetic anhydride or acetyl chloride. The infrared analyses of samples prior to each test indicated that the alcohol content (around 0.10%) following Amberlyst treatment alone was significantly lower than for the untreated TVOPA from blend 100 (0.57%).

(C) As a result of these studies, the procedure for TVOPA production was modified to include treatment in the ion-exchange column containing Amberlyst-15, and a maximum value of 0.06 units for the 5.96 μ infrared absorbance became a part of the TVOPA specifications.

Table XIV. (C) Infrared Analyses and Decomposition Rates for TVOPA Blend 100 (U)

Tess:	Infrared Spectrometer Analysis ²					Adiabatic Heating Rate at 143°C (cal/g-sec)	Comments
	OH (%) ¹	C=C (%) ¹	NONF (%) ¹	5.72μ (AU)	5.96μ (AU)	6.23μ (%)	6.40μ (AU)
348	0.57	nil	1.00	0.092	0.108	0.29	nil
349	trace	nil	0.41	0.027	0.038	0.21	nil
351	nil	nil	0.25	0.014	0.033	0.17	nil
352	0.41	nil	0.70	0.094	0.10	0.27	nil
353	0.10	nil	0.52	0.078	0.045	0.26	nil
355	0.12	nil	0.020	0.010	0.022	0.24	nil
359	trace	nil	trace	(3)	0.029	0.23	nil
361	trace	nil	trace	(3)	0.029	0.17	nil
364	trace	nil	trace	(3)	0.027	0.21	nil
366	trace	nil	0.40	(3)	0.038	0.23	nil
369	0.62	nil	1.45	0.097	0.108	0.26	nil

¹Percent by weight²See Appendix for explanation of tabulated values.³Peak at 5.72μ interferes; acetate ester

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Section VI. (C) ADIABATIC DECOMPOSITION OF NFPOH (U)

(C) Early in the scale-up program for the manufacture of NFPA and TVOPA, the procedure at these Laboratories for producing NFPA included at one stage the isolation of neat NFPOH containing a small amount of zinc chloride, a transesterification catalyst. After an accident in which a container of NFPOH exploded during overnight storage following a stripping operation, adiabatic decomposition tests were conducted to compare the thermal stability of NFPOH with that of TVOPA. Since a high adiabatic heating rate was expected for the NFPOH, the tests were started at 50°C. One test was performed using a sample of NFPOH, and a second test used a sample of the same batch of NFPOH to which 5% by weight zinc chloride had been added. Figure 11 shows the adiabatic heating rates for two previously discussed TVOPA tests for comparison with the heating rates for the tests involving NFPOH. Clearly, the adiabatic heating rate for NFPOH is several orders of magnitude higher than that of TVOPA. Moreover, the presence of 5% zinc chloride in NFPOH significantly increased the heating rate of NFPOH. The manufacturing process for NFPA was altered to eliminate the isolation of neat NFPOH.

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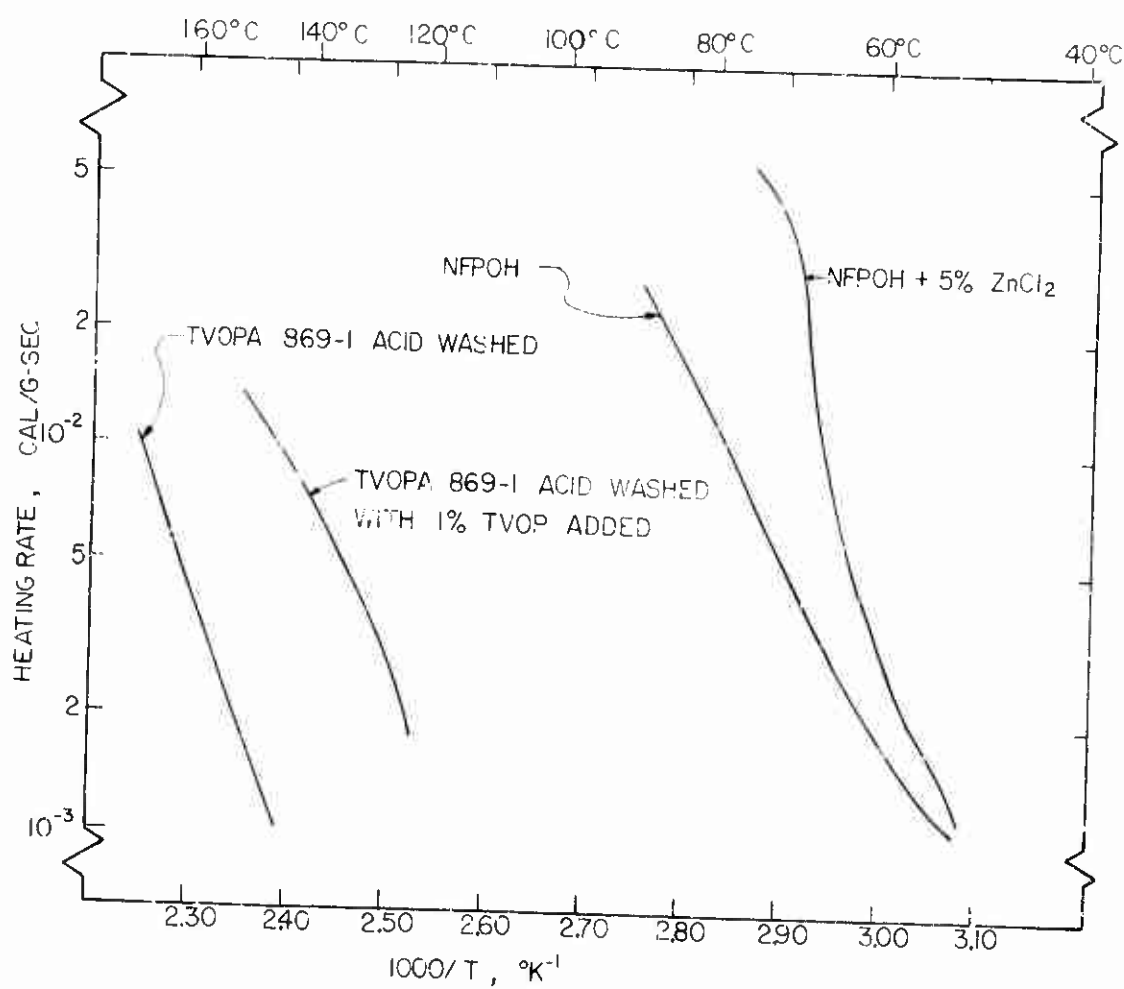


FIGURE 11. (C) ADIABATIC DECOMPOSITION OF NFPOH (U)

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Section VII. (C) THERMAL STABILITY EVALUATION OF RH-SE-TYPE PROPELLANTS (U)

(C) The search for an improved crosslinking system resulted in replacement of the HPMA-HMDI system used in RH-SB-type propellants with an acrylic acid (AA)-diepoxide system used in RH-SE-type propellants. The prepolymer used in the RH-SE-type propellants consisted of an NFPA-acrylic acid copolymer which was crosslinked in propellant with Union Carbide's Epoxide 221. The results from small-scale fissuring tests encouraged the development of the latter system. RH-SE-103 propellant fissured at 80°C in approximately 40 hr, while RH-SB-103 propellant consistently fissured in less than 7 hr at the time of the comparison. At 70°C, RH-SB-103 propellant still fissured in less than 7 hr, while RH-SE-103 propellant fissured in approximately 200 hr. In these preliminary small-scale tests, the prepolymer for the RH-SE-103 propellant consisted of a 94/6 weight ratio of NFPA/AA, and the ratio of epoxide equivalents/acid equivalents varied from 1:1 to 2:1. The AA-diepoxide crosslinking system was selected for further development, and the HPMA-HMDI system was abandoned.

(U) Following the selection of the AA-diepoxide crosslinking system for further development, scale-up of the manufacture of raw materials and propellant processing facilities within these Laboratories made large quantities of propellant available for evaluation. Consequently, the 2-in.-cube fissuring test was used extensively for comparing the thermal stability of propellants.

(C) Numerous batches of RH-SE-103 propellant were prepared for various purposes, and one or two 2-in. cubes were cast from each batch for quality control fissuring tests. In addition, several batches of propellant were prepared specifically for fissuring studies in an effort to correlate time-to-fissure with other variables. The data obtained during these fissuring studies support the following conclusions:

- (1) the use of ferric acetylacetonate (FeAA) curing catalyst in RH-SE-103 propellant decreases the time-to-fissure;
- (2) the time-to-fissure for propellant is increased by increasing high temperature tensile strength;
- (3) the absorption of moisture during ambient temperature storage reduces the time-to-fissure of RH-SE-103 propellant; and

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- (4) the storage of RH-SE-103 propellant in the presence of n-butyl ferrocene vapors results in serious degradation of propellant mechanical properties.

(U) Fissuring studies using several temperatures and cube sizes revealed cube dimensions which would never fissure at various temperatures. These data were used to formulate a model for predicting propellant shelf life at normal service temperatures.

1. (C) Effect of FeAA and Physical Properties on Propellant Fissuring (U)

(C) Early in the development of RH-SE-type propellant, physical properties were varied by altering three primary ratios—namely, NFPA/AA, epoxide/AA, and epoxide/FeAA. FeAA was used as a curing catalyst. However, the addition of FeAA to TVOPA samples had previously been observed to increase significantly the adiabatic heating rate of TVOPA, and its presence in propellant was suspected to shorten the time-to-fissure. A first attempt to investigate the effect of FeAA on time-to-fissure involved 2-in. cubes of RH-SE-103 propellant from Batches 1036 and 1037. Both batches included the same lots of raw materials and were formulated to have essentially equal physical properties; Batch 1036 contained no FeAA. The TVOPA used was unpurified; treatment in the column of Amberlyst had not become a standard procedure at the time these batches were prepared. Only two cubes were made from each batch; one cube from each batch was tested at 70°C, the other at 80°C. Batch formulation, physical properties, and fissuring results are included in Table XV. No difference in fissuring times was observed at 80°C since cubes from both batches fissured in less than 200 hr. However, at 70°C the fissuring times were significantly different, and Batch 1037, containing FeAA, had the shorter time.

(C) Investigation of the effect of FeAA curing catalyst and physical properties on the fissuring performance of RH-SE-103 propellant was continued using three batches of propellant made from the same lots of raw materials. TVOPA treated in the column of Amberlyst-15 and AP coated with Alum-C were used in all three batches. Batch 1041 and 1042 were formulated to give approximately equal physical properties so that the effect of FeAA could be studied. Batch 1044 was formulated to give significantly lower tensile strength by using a lower mole-equivalents ratio of epoxide/acrylic acid. The data in Table XV indicate that the weaker propellant (Batch 1044) fissured in less time than the propellant with

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Table XV. (C) Cube Fissuring Data for RH-SE-103 Propellant (U)

Batch Number	NFPA/AA ²	Epox/AA ³	Epox/FeAA ²	Physical Properties ¹			Hours to Fissure	
				-40°F	77°F	140°F	70°C	80°C
1036	94/6	1.5/1	No FeAA	-	93/32	54/32	630-700	110-200
1037	94/6	1.15/1	5/1	-	89/32	59/29	285-365	110-200
1041	95/5	1.15/1	5/1	410/18	69/27	46/23	>450 ⁴	240-290
1042	95/5	1.5/1	No FeAA	417/16	64/26	45/25	>670 ⁴	270-335
1044	95/5	1.05/1	20/1	266/21	31/55	16/54	>7000 ⁴	330-380
1061	96/4	1.25/1	20/1	291/30	47/44	29/30	1180-1220	400-450
1062	96/4	1.5/1	No FeAA	-	68/33	42/29	900-975	<75
1063	96/4	1.5/1	20/1	-	77/33	40/30	>5200	100-165
							>5200	90-140
							>5200	65-115
							>5200	<90
							>5200	630-670
							>5100	830-930
							>5100	645-695
							>5100	190-255
							>5100	170-235
							>5100	145-190

¹Maximum stress (psi)/strain at maximum stress (%) at 2 in./min crosshead rate

²Weight ratio

³Mole equivalence ratio

⁴Cubes were removed from oven before fissures appeared

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better physical properties. The fissure-time at 80°C for Batch 1041 containing FeAA was slightly shorter than for Batch 1042 which contained no FeAA. At 70°C, cubes of Batch 1041 were removed for various purposes before fissures developed. A single cube from Batch 1042 was stored at 70°C for over 7000 hr (more than 9 months) without fissuring. After the cube was removed from the oven, it was dissected and found to be very hard, testifying to plasticizer loss or some post-cure phenomenon. A 2-in. cube from Batch 1044 lasted about 1200 hours at 70°C before fissures were observed. At the time of these studies, a maximum of four cubes had been available for fissure testing from a single batch, and from most batches only one or two cubes had been available. Although the data available at this point suggested that FeAA reduced the time-to-fissure in RH-SE-103 propellant, sufficient evidence had not been accumulated to eliminate its use.

(U) In a later investigation intended to elucidate the propellant hardening phenomenon, accurate weighing of 2-in. cubes before and after the elevated temperature storage revealed that only 1% weight loss occurred during 1000 hr at 80°C. Since appreciable cube weight loss did not occur, plasticizer loss could not have been the primary cause for the hardening phenomenon.

(C) The first large batches of RH-SE-103 propellant prepared to investigate the effects of FeAA content and physical properties on time-to-fissure of propellant were Batches 1061, 1062, and 1063. The batches included the same lots of raw materials and used 96/4 NFPA/AA copolymer in the binder. Twelve 2-in. cubes from each batch were available for fissure testing. Batches 1062 and 1063 were formulated to give approximately equal physical properties so that the effect of FeAA could be observed, and Batch 1061 was formulated to give a weaker propellant so that the effect of physical properties could be established. The cubes were placed in the ovens at staggered time intervals and removed periodically for X-ray. Time-to-fissure for cubes placed in the ovens within a week after delivery are included in Table XV. Comparison of the fissuring data for Batches 1062 and 1063 confirms that FeAA has a pronounced adverse effect on fissuring performance, and comparison of the data for Batches 1061, 1062, and 1063 confirms that the weaker propellant (Batch 1061) had shorter fissure time than the stronger propellant (Batches 1062 and 1063). Following this evidence, FeAA was no longer used as a curing catalyst for NF propellant, and the desirability for improving the high temperature tensile strength of propellant was clearly evident.

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(C) Increased high temperature tensile strength for RH-SE-103 propellant (without sacrificing low temperature elongation) was realized by modifying the manufacturing procedure for NFPA/AA copolymer. The improved manufacturing process, referred to as the incremental addition process [3], resulted in a higher average molecular weight copolymer with a more narrow molecular weight distribution which was responsible for the increased tensile strength at elevated temperatures as well as increased elongation at low temperatures. Propellant cubes containing copolymer made by the incremental addition process showed much less hardening during high temperature storage than similar cubes containing batch process copolymer. Physical properties and fissure times for propellant containing copolymer made by the incremental addition process are presented in Table XVI.

Table XVI. (C) Cube Fissuring Data for RH-SE-103 Propellant with Copolymer Made by the Incremental Addition Process (U)						
Batch Number	NFPA/AA ¹	Epcx/AA ²	Physical Properties ³			Hours to Fissure at 80°C
			-40°F	77°F	140°F	
1132	96/4	1.5/1	501/31	86/37	60/34	> 1500 ⁴ (3 cubes)
1138	96/4	1.5/1	633/22	84/37	65/31	> 1650 ⁴ (2 cubes)
1149	96/4	1.5/1	625/27	89/32	63/30	> 2300 ⁴ (2 cubes)
1150	96/4	1.5/1	645/26	83/31	62/29	> 5000 ⁵
1152 ⁶	96/4	1.5/1	597/28 ⁶	67/42 ⁶	52/38 ⁶	550-600 >5000 ⁵
¹ Weight ratio ² Equivalence ratio ³ Maximum stress (psi)/strain at maximum stress (%) at 2 in./min crosshead rate. ⁴ Cubes were dissected, no fissures were found; hardening was much less noticeable than in previous propellants. ⁵ Test continuing ⁶ Batch 1152 had a high water and ethyl acetate content which caused the poor mechanical properties and scattered fissuring results. The binder for the batch was stripped without stirring because of equipment problems.						

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2. (C) Effect of Moisture and Volatile Contaminants on Propellant Fissuring (U)

(C) Fissuring data for cubes of RH-SE-103 propellant made from Batches 1061, 1062, and 1063 which were placed in the fissuring ovens soon after their manufacture have been discussed above. Cubes from the same batches which were stored several days under ambient conditions before they were placed in the fissuring ovens fissured in a much shorter time. A complete summary of fissuring data for 2-in. cubes from these batches which were tested at 80°C is available in Table XVII. The reduction of time-to-fissure with longer periods of ambient storage is apparent.

(C) Absorption of moisture from the atmosphere was postulated to be responsible for the reduction in fissuring time of cubes stored under ambient conditions. Although a standard practice of wrapping all cubes in aluminum foil had been followed carefully, the foil was not sealed, and over a period of time moisture could conceivably diffuse into the propellant. To check this hypothesis, several 2-in. cubes of RH-SE-103 propellant from Batch 1120 were stored under ambient conditions and started in the 80°C fissuring test at approximately 5-day intervals. In addition, one cube was stored in a desiccator over water for 65 days before it was placed in the fissuring oven, and two cubes were placed in a desiccator over phosphorus pentoxide for 70 days before the fissure test was started. The dramatic reduction in time-to-fissure with ambient storage is evident from Figure 12 which indicates that fissuring time decreased from about 400 hr to about 100 hr after 6 weeks of ambient storage. Furthermore, the cube stored over water for 65 days fissured in less than 7 hr, while both cubes stored in a desiccator over phosphorus pentoxide for 70 days lasted approximately 400 hr before fissuring. The cube stored over water increased in weight by 0.13% during the 65 days of storage, and the weight of two cubes stored over phosphorus pentoxide decreased by 0.01% during the 70 days of dry storage. These data vividly demonstrate the effect of small quantities of moisture on fissuring performance of RH-SE-103 propellants and indicate the importance of desiccating and sealing rocket motors directly after removal from the curing ovens.

(C) A series of tests was initiated to investigate further the effect of ambient storage conditions and time on the physical properties and time-to-fissure of RH-SE-103 propellant. Several cubes and slabs were prepared from a 50-lb batch of propellant (Batch 1157). Some cubes were placed in the fissuring ovens at 80° and 90°C immediately after delivery, and the remaining cubes

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Table XVII. (C) Ambient Storage Effect on Cube Fissuring Time at 80°C for RH-SE-103 Propellant (U)			
Propellant Batch	Days of Ambient Storage Prior to Testing	Hours to Fissure	Comments
1061	0	90-140	2 small fissures (1/4 in. dia)
	1	65-115	2 small fissures (1/4 in. dia)
	8	<90	5 small fissures
	36	<70	Many small fissures through- out
	36	<70	Many small fissures through- out
	48	<20	Spongy, many small fissures
	49	<30	Many small fissures
1062	0	600-670	1 large fissure
	4	830-930	1 small fissure (1/2 in. dia)
	10	645-695	1 small fissure
	30	<120	1 small fissure
	44	50-00	2 fissures (3/4 in. dia)
	45	130-200	
1063	0	190-255	1 large and 1 small fissure
	1	170-235	1 large fissure
	7	145-190	
	27	<120	Many large fissures through- out
	41	<18	Many small fissures
	42	<30	Many small fissures

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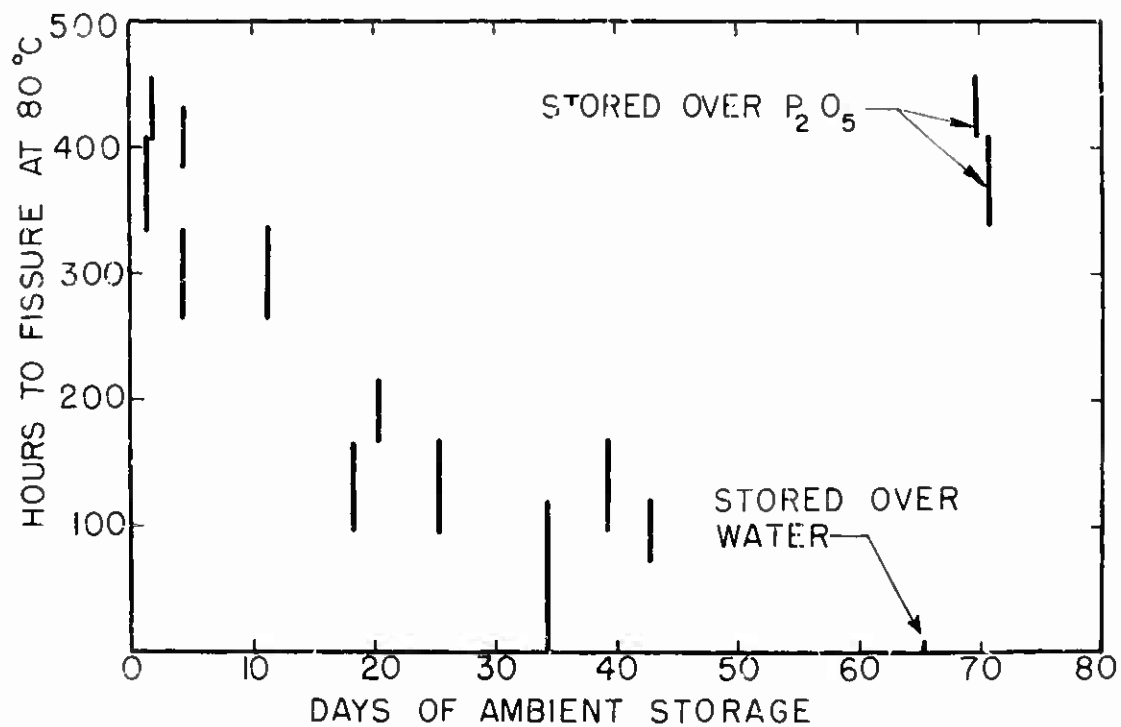


FIGURE 12. (C) EFFECT OF AMBIENT STORAGE ON CUBE FISSURING TIME OF RH-SE-103 PROPELLANT (U)

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were stored (unwrapped) in sealed chambers having 0%, 50%, or 100% relative humidity, all at ambient temperature. Cubes were removed periodically, wrapped in aluminum foil, X-rayed, and placed in fissuring ovens at 80°C and 90°C. Table XVIII includes the 2-in. cube fissuring data obtained to date for this test. After 7-day storage at 100% RH and ambient temperature, the time-to-fissure in 2-in. cubes was less than 30 hr in both the 80° and 90°C ovens. After 12-day storage at 100% RH and ambient temperature, the cubes were badly fissured before they were placed in the test ovens. Cubes placed in the oven immediately after delivery fissured between 400 and 500 hr (17-21 days). These data demonstrate the importance of keeping RH-SE-103 propellant dry.

(C) Physical property surveillance tests were also made to detect any physical property changes on RH-SE-103 propellant resulting from the moisture content of the environment. Data for 30- and 60-day storage at 0%, 50%, and 100% RH and ambient temperature are shown in Table XIX, and 90-day storage data are presented for 0% RH. The mechanical properties of the specimens stored at 100% RH degraded markedly, but only minor changes occurred in the specimens stored at 0% and 50% RH environments. Again, the importance of keeping RH-SE-103 propellant dry was emphasized.

(C) The physical properties surveillance program uncovered a serious incompatibility problem between RH-SE-103 propellant and n-butyl ferrocene (nBF) vapor. Most of the physical properties specimens were stored in sealed chambers containing only RH-SE-103 propellant (and the agent to control relative humidity). A few of the specimens stored at 0% RH, however, were placed in a desiccating cabinet with carboxyl-terminated polybutadiene propellants containing nBF. Table XIX reveals that after 30 days in the presence of nBF vapors, the RH-SE-103 propellant degraded more than that stored at 100% RH and also developed a brittle outer crust. Table XIX also reveals that specimens stored at 0% RH in the absence of nBF vapors did not exhibit the same sort of physical property change, thus confirming the suspected role of nBF. When the problem was discovered (after 30 days of storage) all remaining physical properties samples being stored at 0% RH in the cabinet containing nBF vapors were removed from that cabinet and placed in a chamber which contained only RH-SE-103 propellant. The data in Table XIX indicate that no significant recovery in physical properties occurred for the samples stored for 30 days in the presence of nBF vapors after 30 additional days in the absence of nBF.

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Table XVIII. (C) Effect of Ambient Storage Condition on Cube Fissuring Time (hr) of RH-SE-103 Propellant (Batch 1157) (U)						
Days of Storage	0% RH		50% RH		100% RH	
	80°C	90°C	80°C	90°C	80°C	90°C
0	640-690 470-520 350-425 425-475	40-110 40-110 40-110 40-110				
7	385-455	30-120	290-335	30-120	<30	<30
12	500-550	<50	95-165	<50	¹ —	¹ —
26	385-430 ³ 385-430 430-500 ³ 420-500	23-45 23-45	<47 <47 47-95 ³ 47-95 ³		² —	² —
40	425-500	<96	<48	<48		
55	400-470 470-520	17-65 17-65	<17 17-65	<17		
68	385-430	50-95	<50			
82	385-430 215-265	50-95 50-95				
110	385-430 430-500	50-75 50-75				
¹ Cubes stored at 100% RH for 12 days fissured during ambient storage. ² Cubes wrapped in aluminum foil and stored 26 days at ambient temperature and 100% RH fissured during ambient storage. ³ Cubes wrapped with aluminum foil during ambient storage.						

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Table XIX. (C) Effect of Relative Humidity on Mechanical Properties of RH-SE-103 (Batch 1157) (U)			
	$\frac{\sigma(\text{psi})^*}{\epsilon(\%)}$ at -40°F	$\frac{\sigma(\text{psi})^*}{\epsilon(\%)}$ at 77°F	$\frac{\sigma(\text{psi})^*}{\epsilon(\%)}$ at 140°F
Initial data (0 days)	514/20	68.0/32	52.0/31
32 days at 0% RH	558/16	74.3/30	44.4/27
60 days at 0% RH	600/19	73.6/30	43.7/25
90 days at 0% RH	639/16	75.2/31	46.5/30
30 days at 50% RH	493/22	64.9/30	44.9/27
60 days at 50% RH	528/22	64.7/34	43.9/29
30 days at 100% RH	439/12	36.1/26	21.4/11
60 days at 100% RH	588/5	18.3/25	7.6/7
30 days at 0% RH with nBF	507/13	29.6/<5	14.7/<5
60 days at 0% RH (30 days with nBF)	545/?	26.9/<5	23.5/<5
*Maximum stress (psi)/strain (%) at maximum stress at 2 in./min crosshead rate.			

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(C) After the adverse effect of moisture absorption on fissuring performance of RH-SE-103 propellant had been demonstrated, several exploratory experiments were undertaken to determine the amount of water in TP-binder⁹ as manufactured, to define techniques for its removal, and to determine the effect, if any, of its presence on fissuring behavior and physical properties of propellant.

(U) A listing of significant results related to water analysis for TP-binders and the effectiveness of water removal techniques is presented in Table XX. In summary, items 1 and 2 and items 3 and 9 in Table XX indicate that stripping the binder at room temperature is insufficient to remove the small quantities of water present, while nitrogen sparging seems to produce a significant change (items 8 through 19). Items 15 through 19 indicate that sparging with nitrogen dried by passing through a column of Drierite^{®10} and then through a liquid nitrogen trap is essentially complete after only 5 hr when the binder is at 70°C. Items 12 through 14 indicate that nitrogen dried by passing through a column of Drierite is less effective as a sparging agent than nitrogen dried by passing through a column of Drierite and then through a liquid nitrogen trap.

(C) It might seem that 0.2% water in TP is a negligibly small quantity. On a mole basis, however, this amount of water corresponds to approximately one-half the number of moles of AA in the copolymer. If the water is reactive with the diepoxide crosslinker, a significant effect on crosslink density and physical properties might be anticipated.

(C) In a related experimental program the effects of moisture and other volatile contaminants which may be present when propellant is mixed and cast were investigated. Analysis of several batches of binder indicated that production TP-binders may contain as much as 0.2% water and as much as 0.6% ethyl acetate. Nitrogen sparging was effective in reducing both the water and ethyl acetate content of TP-binders. A series of experiments was conducted using different batches of propellant made with the same lots of raw materials to determine the effect of water and ethyl acetate (a solvent used in processing) in TP on fissuring and physical

⁹ TP-binder is the designation assigned to the mixture of NFPA copolymer and TVOPA plasticizer.

¹⁰ Trademark of W. A. Hammond Drierite Company, Xenia, Ohio.

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Table XX. (U) Effect of Nitrogen Sparging on Water Analysis of TP-Binders			
Item	Batch Number	Wt. % H ₂ O	Remarks
1	TP-11-1030	0.18	As received, no treatment
2	TP-11-1030	0.18	Additional strip of item 1 (16 hr, 1 mm Hg, 25°C)
3	TP-11-1030R	0.22	Item 1 redissolved in ethyl acetate and restripped by standard procedure
4	TP-11-1030R	0.22	Additional strip of item 3 (16 hr, 1 mm Hg, 25°C)
5	TP-12-1003	0.16	As received, no treatment
6	TP-12-1003	0.11	Item 5 sparged with N ₂ from cylinder as received (60 hr at 60°C)
7	TP-12-1003	0.14	Item 5 with 4% (based on TP) 3A molecular sieve added to ethyl acetate before stripping
8	TP-11-1038	0.22	As received, no treatment
9	TP-11-1038	0.16	Additional strip of item 8 (16 hr, 1 mm, 25°C)
10	TP-11-1038	0.12	Item 8 sparged with N ₂ from cylinder as received (16 hr at 70°C)
11	TP-11-1038	0.037	Item 8 sparged with N ₂ passed through Drierite (16 hr at 70°C)
12	TP-11-Blend	0.18	A blend of several combined batches, as received
13	TP-11-Blend	0.11	Sparged 16 hr at 70°C with N ₂ passed through Drierite
14	TP-11-Blend	0.058	Same as item 13 after 24 hr
15	TP-11-1034	0.15	As received
16	TP-11-1034	0.040	5-hr sparge with N ₂ passed through Drierite column and a liquid N ₂ trap; TP was at 70°C
17	TP-11-1034	0.047	Same as item 16. Sparged 10 hr
18	TP-11-1034	0.042	Same as item 16. Sparged 22 hr
19	TP-11-1034	0.043	Same as item 16. Sparged 28 hr

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properties. RH-SE-103 propellant Batch 1137, which was the control batch, used production grade TP-12-1006 binder. Batch 1140 used TP which had been dry-nitrogen sparged overnight at 70°C; Batch 1141 used the same sparged TP with 1% ethyl acetate (by weight) added; and Batch 1147 used the sparged TP with 0.2% water (by weight) added. The times-to-fissure for 2-in. cubes from all batches were so close that the test was somewhat inconclusive (Table XXI); however, a study of the data sheds some light on the fissuring behavior. Table XXI indicates that TP-12-1006 which was used in these experiments had about the lowest water and ethyl acetate content ever obtained in production material—about 10 times less than has been observed in some cases. In fact, TP-12-1006, at the time it was used to make the control batch, had a water and ethyl acetate content about as low as was obtained using dry-nitrogen sparging on previous TP batches (Table XX).

(C) As a result of scheduling delays, two weeks elapsed between the casting of the control batch and sparging of the remaining batches. During this time the water content of the TP increased from 0.025% to 0.043%. The subsequent nitrogen sparging simply reduced the water content to 0.023%, which is approximately the same as the TP contained when the control batch was cast. In addition, Table XXI indicates that the elevated temperature mechanical strength for Batches 1137 and 1140 was almost identical—further explaining the very similar fissuring performance. The physical property data of Table XXI suggest that ethyl acetate is an extremely effective plasticizer, and the slightly reduced fissuring times for Batch 1141 (340-380 hr for Batch 1141 compared with 330-460 hr for Batch 1140) may have been due entirely to reduced mechanical strength.

(C) The water added to the sparged TP caused insignificant reduction in fissuring time for Batch 1147. In the light of data previously discussed concerning the detrimental effect of moisture pickup during ambient storage, it is suspected that the water added to the TP never got into the propellant. Two likely explanations are as follows: (1) the curing reaction used the water in preference to crosslinking, or (2) the vacuum mixing and casting procedure was effective in removing water from the TP. Very similar mechanical properties were obtained from propellant made with the sparged material with and without water, indicating that water did not affect the crosslinking. Therefore, it is suspected that vacuum mixing and casting are effective in removing water. It should be noted, however, that for larger batches, vacuum mixing and casting may be less effective in removing water and other

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volatile contaminants. On the basis of previous studies which demonstrated the adverse effect of moisture on cube fissuring behavior and the present study which has indicated reduced propellant strength in propellant containing only 1% ethyl acetate, it is believed that any amount of these volatile materials has an adverse effect on fissuring performance, and sufficient control should be exercised to reduce their levels in RH-SE-type propellant as much as is practical. Experience has shown that stirring during stripping of TP-binder is necessary for satisfactory removal of volatile contaminants.

3. (C) Effect of Cube Size and Temperature on Time-to-Fissure (U)

(C) Tests were conducted recently to determine the effect of cube size and temperature on time-to-fissure of RH-SE-103 propellant, the formulation selected for scale-up. Several 4-in., 3-in., 2½-in., 2-in., 1½-in. and 1-in. cubes were prepared from a 50-lb batch of propellant (Batch 1151). The propellant used in this test used very good ingredients, embodying all the improvements discussed above, except copolymer made by the incremental addition process was not used. Fissuring tests were conducted at oven temperatures of 60°, 70°, 80°, and 90°C. A summary of the data is presented in Table XXII. The data reflect the pronounced effect of both cube size and temperature on fissuring time. Data from the tests allow determination of a cube size which will never fissure at a specified temperature. A mathematical model for predicting propellant shelf life at service temperatures has been developed which correlates the data well. The model and predictions of propellant shelf life are discussed in a separate report [1]. The service life predicted for RH-SE-103 propellant is judged to be more than adequate for world-wide Army requirements. Additional tests using propellant containing copolymer made by the incremental addition process are also planned.

4. (U) Adiabatic Decomposition of RH-SE-103 Propellant

The number of adiabatic decomposition tests conducted with RH-SE-103 propellant has been much smaller than the number of tests performed with previously discussed compositions. Because larger quantities of RH-SE-103 propellant have been available, more emphasis has been placed on the cube fissuring tests since results are more directly applicable for predicting propellant shelf life. For comparison with RH-SA-103 and RH-SB-103 propellant, the adiabatic heating rate for a typical test involving RH-SE-103

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Table XXI. (C) Effect of Volatile Impurities in TP-Binder on Propellant Physical Properties (U)					
Propellant Batch	σ/ϵ^1 at -40°F	σ/ϵ^1 at 77°F	σ/ϵ^1 at 140°F	Wt. % Water in TP	Wt. % Ethyl Acetate in TP
Batch 1137 unsparged TP	440/21	61.6/42	47.7/38	0.025 (when cast)	<0.1
Batch 1140 sparged TP	490/25	66.2/36	47.6/37	0.023 (0.043 before sparging)	<0.1
Batch 1141 sparged TP with 1% ethyl acetate added	434/26	47.7/50	34.0/52	0.023	1
Batch 1147 sparged TP with 0.2% H ₂ O added	496/22	68.6/40	44.3/40	0.023+0.200= 0.223 (when cast)	<0.1
¹ Maximum stress (psi)/strain at maximum stress (%) at 2 in./min crosshead rate.					

Table XXII. (C) Effect of Cube Size and Temperature on Time-to-Fissure for RH-SE-103 Propellant (U)				
Cube Size (in.)	Time to Fissure (hr) **			
	at 60°C	at 70°C	at 80°C	at 90°C
4	2110-2445 2110-2445	430-500 430-500		
3	>3300† >3300†	770-840 >840* 935-1005	95-165 95-165 95-165	
2½		>3300† >3300†	95-165 95-165 95-165	22-46 22-46 22-46
2		>2700† >2700†	430-500 600-670 600-670 600-670	45-70 23-47 45-70 22-46
1½			>2600† >2600† >2600†	95-165 70-140 70-140
1				>3500† (5 cubes)
*Test stopped; no fissure found **The first number of each entry indicates hour of storage at the last X-ray showing no fissure; the second number indicates hours of storage at the time of the first X-ray showing a fissure. †Test continuing				

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is shown in Figure 7. Adiabatic decomposition test reproducibility for RH-SE-103 propellant was very similar to the reproducibility previously reported for other propellants; that is, within-batch reproducibility was excellent, but batch-to-batch variations were evident for propellant batches containing different lots of raw materials. Typical kinetic parameters and heating rates obtained for RH-SE-103 propellant are shown in Table XXIII.

Table XXIII. (U) Kinetic Parameters for RH-SE-103 Propellant			
Batch	E Kcal/mol)	QZ (cal/g-sec)	Heating Rate at 143°C (cal/g-sec)
1169	25.0	2.981×10^{10}	2.15×10^{-3}
	24.9	2.335×10^{10}	1.90×10^{-3}
1082	25.1	1.399×10^{10}	0.77×10^{-3}
1062	26.4	1.442×10^{11}	1.91×10^{-3}
1076	26.1	8.744×10^{10}	1.67×10^{-3}

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Section VIII. (C) ADIABATIC DECOMPOSITION OF NF PROPELLANT BINDERS (U)

(C) An intermediate product in the manufacture of typical TVOPA/NFPA propellants is the binder. The binders employed in RH-SE-type propellants contain a copolymer of NFPA/AA and TVOPA. Since a major portion of the thermal stability evaluation of TVOPA/NFPA propellants has involved RH-SE-103 propellant which contained a 2/1 weight ratio of TVOPA/copolymer, this section will be restricted to binders containing this ratio of plasticizer to copolymer.

(C) Many adiabatic decomposition tests have been conducted using binders containing a 95/5 weight ratio of NFPA/AA (designated TP-11) and a 96/4 weight ratio of NFPA/AA (designated TP-12). Figures 13 and 14 show the adiabatic heating rates obtained from several tests using TP-11 and TP-12, respectively. These figures demonstrate the similar shape of adiabatic heating curves for binder experiments and, hence, substantiate the reasoning for reporting the heating rates at a single temperature. The temperature of 143°C ($1000/T^{\circ}K=2.40$) was chosen for reporting the adiabatic heating rates for TP-binders since it is near the center of the temperature span covered during a typical test. The heating rates for TP-11 and TP-12 binders at 143°C are tabulated in Table XXIV and XXV, respectively. Table XXV also includes the heating rates for TP-12E binders which contain copolymer manufactured by the incremental addition process discussed earlier. Although only a limited amount of data has been accumulated for TP-12E binder, a comparison of Tables XXIV and XXV suggests that TP-12E is slightly more stable than TP-11 or TP-12. Better fissuring performance and better physical properties for RH-SE-103 propellants containing copolymer manufactured by the incremental addition process have been cited previously.

(C) To observe the effect of an alcohol on the heating rate of TP binder, 1% by weight ethylene glycol was added to a sample of TP-12-1006 prior to the adiabatic decomposition test. The heating rate at 143°C for the resulting sample was 5.9×10^{-3} cal/g-sec. Table XXV shows that in test 502 the adiabatic heating rate for TP-12-1006 binder (without ethylene glycol) was 2.1×10^{-3} cal/g-sec. This test confirmed the suspected role of alcohols in accelerating the decomposition of NF materials. Earlier adiabatic decomposition tests in which TVOPA had been salted with small quantities of water and volatile alcohols produced very little change in the heating rate. In view of this more recent test with ethylene

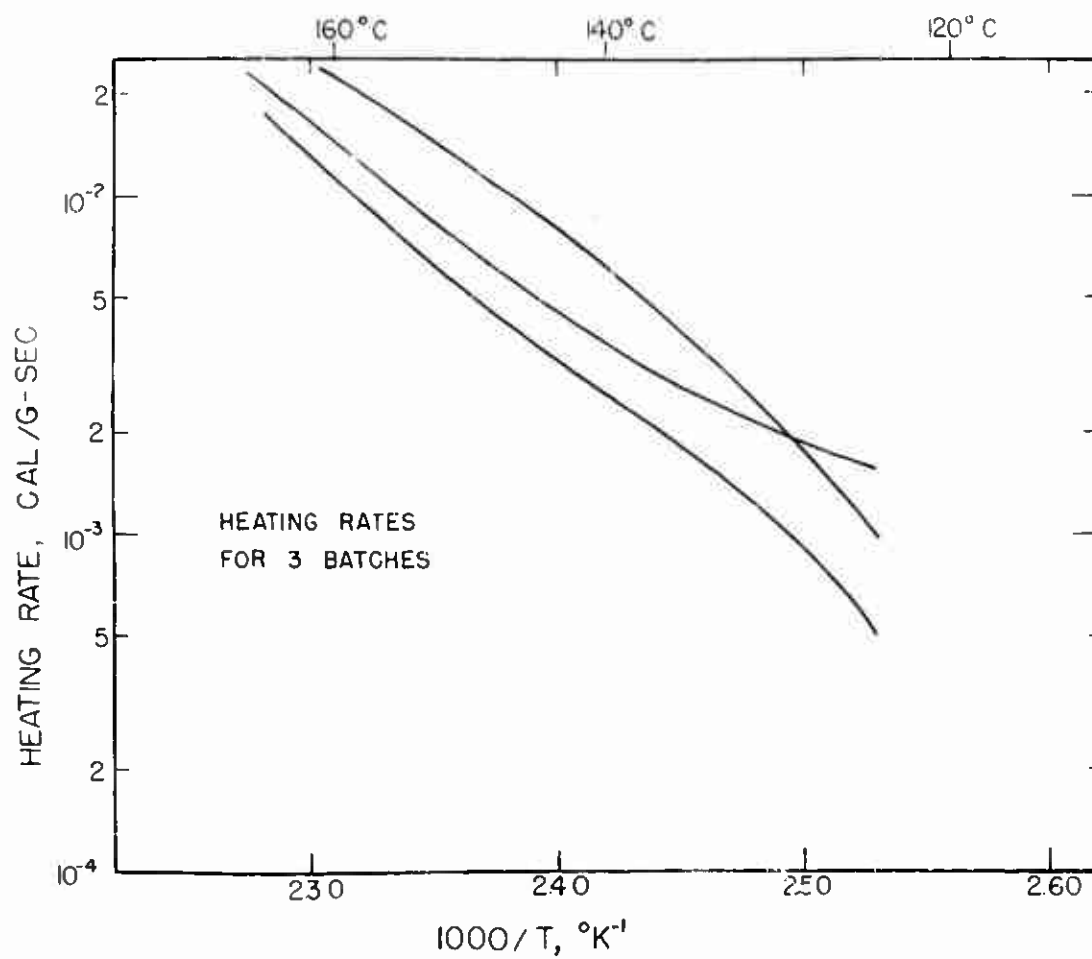


FIGURE 13. (U) ADIABATIC DECOMPOSITION OF TP-11 BINDER

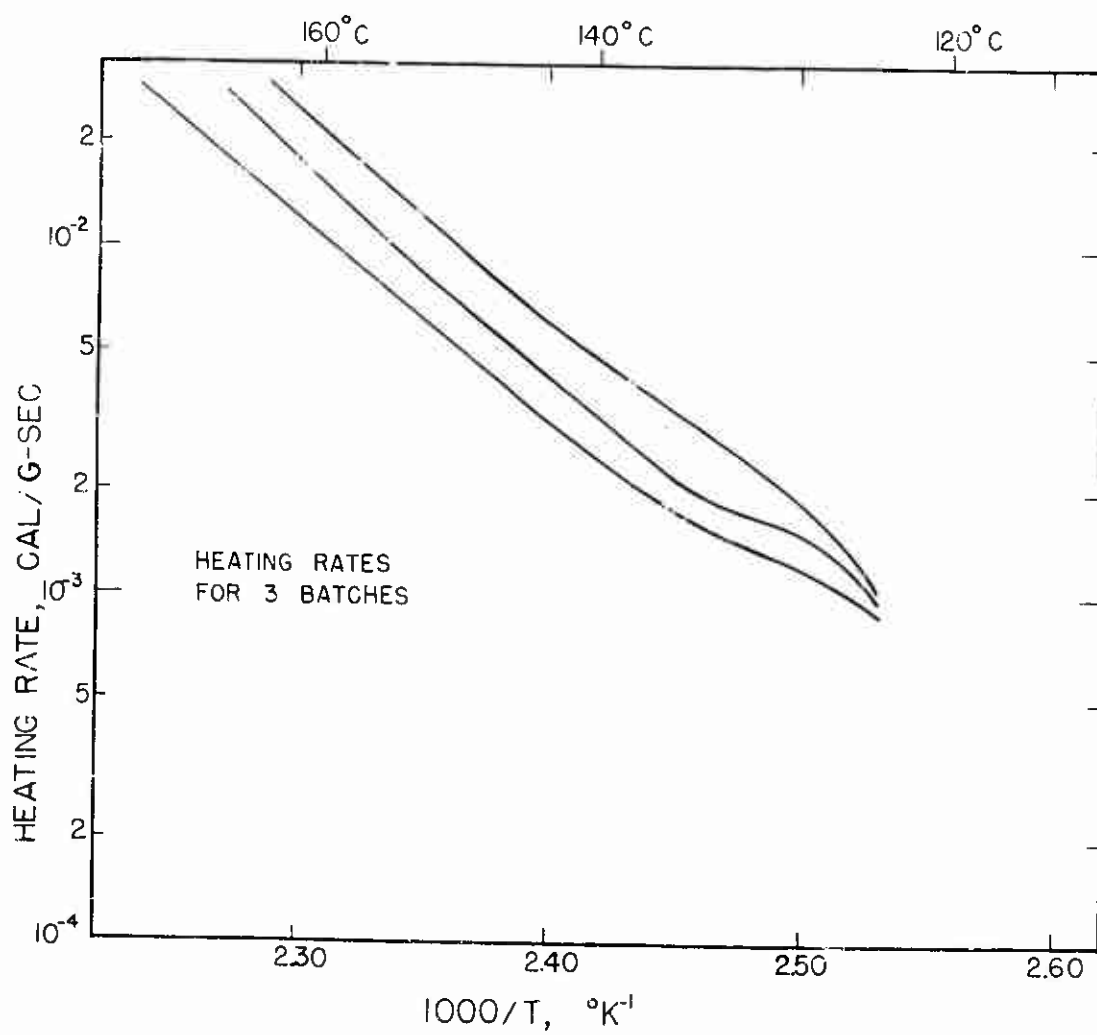


FIGURE 14. (U) ADIABATIC DECOMPOSITION OF TP-12 BINDER

Table XXIV. (U) Adiabatic Decomposition Rate of TP-11 Binder					
Test	Batch No.	Adiabatic Heating Rate at 143°C (cal/g-sec)×10 ³	Test	Batch No.	Adiabatic Heating Rate at 143°C (cal/g-sec)×10 ³
313	1002	6.0	420	1032	2.1
330	1003	4.5	432	1033	4.0
333	1000	3.3	438	1035	4.5
356	1012	3.4	441	1036	3.4
378	1014	3.3	443	1038	3.6
379	1015	6.4	445	1037	1.5
385	1019	2.9	448	1039	4.2
387	1009	3.8	449	1040	3.6
391	1016	2.1	450	1038	3.1
392	1017	3.3	464	1040	5.7
393	1018	4.6	466	1041	8.6
394	1019	4.8	470	1042	2.7
396	1020	2.1	471	1043	3.3
404	1024	5.6	480	1045	2.6
405	1025	4.7	481	1046	3.1
413	1027	5.7	482	1047	5.4
414	1026	2.3	487	1048	3.3
415	1028	2.7	491	1044	1.5
416	1029	3.1	520	1049	5.2
417	1030	3.3	521	1050	3.5
418	1031	2.3			
			Average 3.8		
			RMS deviation ± 1.4		

Table XXV. (U) Adiabatic Decomposition Rate of TP-12 Binder					
Test	Batch No.	Adiabatic Heating Rate at 143°C (cal/g-sec)×10 ³	Test	Batch No.	Adiabatic Heating Rate at 143°C (cal/g-sec)×10 ³
380	1001	1.5	488	E-100	4.5
381	1002	3.5	490	E-101	2.5
383	1018	4.9	492	E-102	8.3*†
395	1003	2.5	493	E-103	1.2*
422	1003	2.3	499	E-104	0.9
446	1003	2.6	507	E-105	1.1
456	1004	3.2	515	E-107	3.9
484	1005	1.2	523	E-107A	3.7
497	1006	2.1	524	E-109	2.1
500	1007	6.0	<div>Average2.5</div> <div>RMS deviation±1.31</div>		
502	1006	2.0			
503	1006	2.1			
505	1009	5.2			
514	1008	3.2			
522	1010	3.2			
526	1011	4.3			
527	1012	6.2			
Average3.3					
RMS deviation±1.5					

*0.9% NFPOH in NFPA used
 †Poor TVOPA used. Rate omitted from average.

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glycol in TP binder, it is suspected that in the earlier tests with TVOPA the initial temperature for the adiabatic decomposition tests (around 250°F) was sufficiently high to drive off the more volatile impurities before they contributed significantly to the decomposition.

(C) Preliminary experiments indicate that additional improvement in the thermal stability of propellants may be possible through the use of geminal NFPA rather than vicinal NFPA in the binder. The adiabatic heating rates for some typical propellant binders containing 2/1 TVOPA/geminal NFPA are presented in Figure 15. For comparison with Tables XXIV and XXV, Table XXVI includes the heating rate at 143°C for the binders containing geminal NFPA. These data indicate that the average adiabatic heating rate (at 143°C) for six tests using binder containing geminal NFPA was about half the rate for TP-11 and TP-12 binders containing vicinal NFPA; however, only a modest improvement for the binder containing geminal NFPA is observed when compared with TP-12E binder containing vicinal NFPA in which the copolymer is made by the incremental addition process.

Table XXVI. (C) Adiabatic Decomposition Rates of Binder Containing Geminal NFPA (U)			
Test	Sample	Adiabatic Heating Rate at 143°C (cal/g-sec) × 10 ³	Comments
179	TP-MGB-669-11B	1.74	gem-NFPA, acid washed TVOPA 832-1
362	TP-EA-1116-31	0.94	gem-PPAA MB-669-48. 2/1 TVOPA/PPAA
367	TP-EA-1116-32	1.3	TVOPA Blend 100 (acid washed) and gem-NFPA
400	TP-GNFPA-1	1.5	
506	TP-12G-100	2.1	
513	TP-12G-101	2.0	Dark color
Average		1.6	
RMS deviation		± 0.4	

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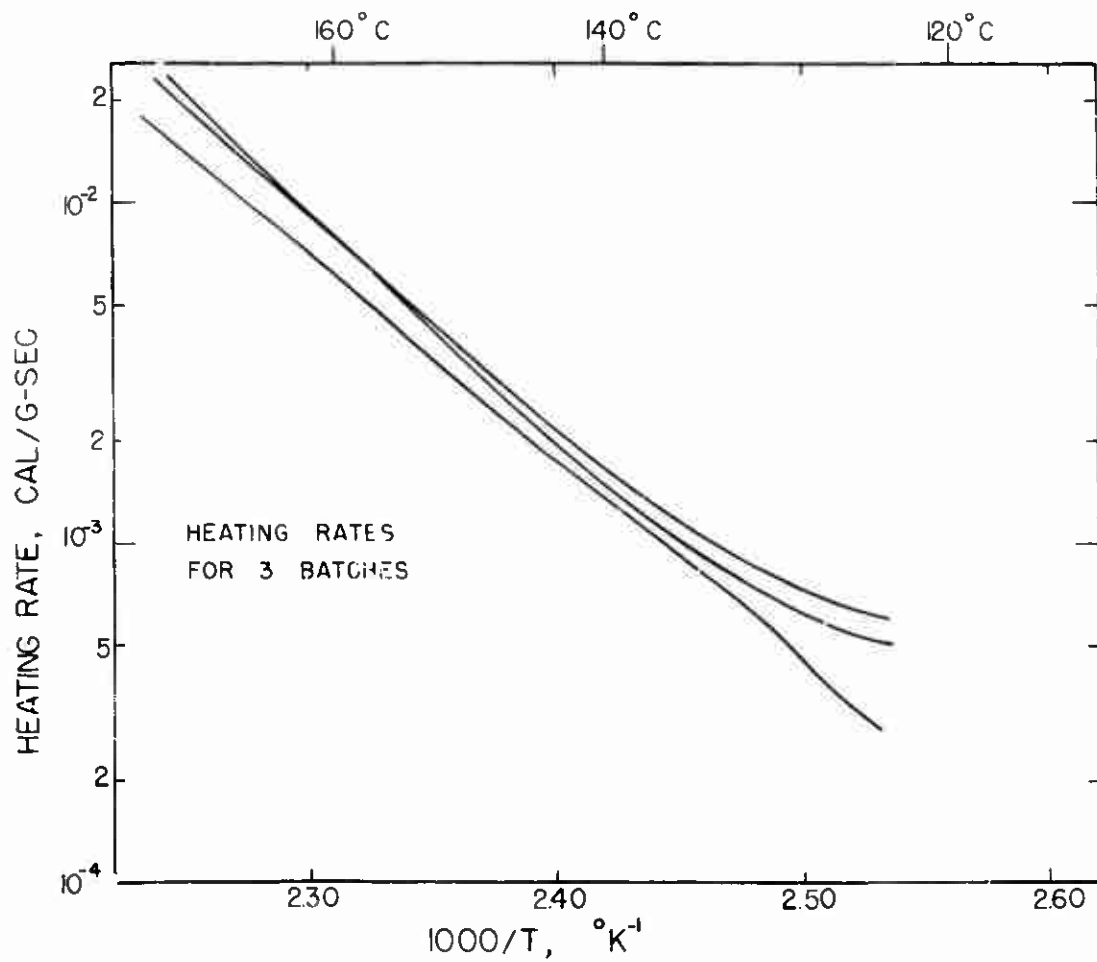


FIGURE 15. (U) ADIABATIC DECOMPOSITION OF BINDER
CONTAINING GEMINAL NFPA

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Section IX. (C) A PRELIMINARY INVESTIGATION OF GEMINAL NF INGREDIENTS (U)

(C) In an effort to characterize the thermal stability of geminal NF formulations, adiabatic decomposition tests were conducted using samples of geminal copolymer (96/4 gem-NFPA/AA) and binder and propellant containing the geminal copolymer. The adiabatic heating rate at 143°C for each sample is shown in Table XXVII. The heating rates for all geminal materials tested were lower than average for their vicinal counterparts. In comparing the heating rates of geminal and vicinal formulations, geminal copolymer (PY-1-7003) demonstrated the most dramatic improvement over its vicinal counterpart, PPAA. Adiabatic decomposition tests with vicinal copolymer typically began at 250°F and proceeded sufficiently fast to reach 320°F in about 70 min. The heating rate at 143°C (the usual temperature at which the heating rate is reported) for vicinal copolymer was about 15×10^{-3} cal/g-sec. Geminal copolymer (PY-1-7003) failed to increase in temperature when a sample was placed in the adiabatic oven at 250°F. After 2 hr at 250°F, the initial temperature was increased manually to 280°F. Even from 280°F, no thermal decomposition occurred through 64 hr. The sample was then removed from the oven and air-cooled; the adiabatic oven control system was thoroughly checked; and the sample was returned to the oven—this time, the initial temperature was set at 320°F. From this temperature, adiabatic decomposition did occur, but quite slowly. The heating rate was extrapolated downwards to a temperature of 143°C for comparison with typical vicinal copolymer and found to be approximately 0.1×10^{-3} cal/g-sec (lower than vicinal copolymer by a factor of 150). This was the first adiabatic decomposition test using a sample of unplasticized geminal NF copolymer; several previous tests had been conducted using geminal copolymer plasticized with a supposedly inert material such as Santicizer^{®11} B-16 or Santicizer-160 to facilitate handling. Before the test using unplasticized geminal copolymer, some reservations were held concerning the extremely low adiabatic heating rates which had been observed during tests with the plasticizer material. The test using unplasticized geminal copolymer demonstrated the remarkable thermal stability of copolymer containing geminal NFPA and thus qualitatively confirmed the results from the tests using plasticizer samples.

¹¹Trademark of Monsanto Chemical Company, St. Louis, Mo.

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Table XXVII. (C) Adiabatic Decomposition Results, A Comparison of Geminal and Vicinal Formulations (U)		
Sample	Adiabatic Heating Rate at 143°C × 10 ³ (cal/g-sec)	Comments
1. PPAA-4-1016 Copolymer	14.	Typical vicinal copolymer for comparing with item 2
2. PY-1-7003 Copolymer	0.1*	Contained 96/4 gem-NFPA/ AA. Sample would not decom- pose adiabatically from initial temperature of 250°F or 280°F. Sample decomposed slowly when started at 320°F. Com- pare with item 1.
3. TP-12-1020 Binder	3.0	Standard binder containing vicinal ingredients for com- paring with item 4. Contained TVOPA batch 122-2
4. TY-1-7003 Binder	1.6	Contained <u>gem</u> -copolymer FY-1-7003 and TVOPA batch 122-2. Compare with item 3.
5. RH-SE-103- 1149	1.5	Typical propellant containing vicinal ingredients with same formulation as item 6
6. RH-Y-1-7001 Propellant	1.0	Contained <u>gem</u> -binder TY-1- 7003. Compare with item 5.
*Heating rate for PY-1-7003 was obtained by extrapolation of data recorded at higher temperatures.		

(C) The adiabatic heating rate for binder (TY-1-7003) containing geminal copolymer was only slightly lower than that for binder made with vicinal copolymer. Similarly, the heating rate for propellant containing geminal copolymer was only slightly lower than that for propellant with vicinal ingredients. Evidently, the incorporation of the vicinal plasticizer, TVOPA, in the binder limits the

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improvement in adiabatic heating rate which can be realized with geminal copolymer. Adiabatic decomposition tests with binder made with geminal copolymer and geminal plasticizer will be conducted when a suitable geminal plasticizer becomes available.

(C) Fissuring tests with two 2-in. cubes of RH-Y-1-7003 propellant (a formulation identical to RH-SE-103 but containing geminal-NF copolymer) continued for more than 1600 hr at 80°C without evidence of fissure. After 1600 hr, one of these cubes was placed in an oven at 90°C and fissured between 100 and 165 hr later. The second cube, which remained in the oven at 80°C, has withstood 2800 hr without fissuring. It is doubtful that this cube will ever fissure since a steady-state concentration of gases evolved during the decomposition has most likely already been reached. Despite the long period of elevated temperature storage, neither of these cubes has hardened appreciably.

(U) Although these preliminary studies have encouraged a more thorough investigation of propellants and binder containing geminal-NF compounds, additional studies will be required to properly assess the merits of producing geminal ingredients on a larger scale. This is primarily due to the economic advantage of producing vicinal ingredients and the significant improvements which have recently been made in vicinal propellant via development of the incremental additon process.

(C) A comparison of the adiabatic heating rates for copolymer (for example, PPAA-4-1016 copolymer in Table XXVII) with the heating rates for TVOPA (Table XIV) indicates that the copolymer is much less stable. The greater thermal stability of TVOPA is largely due to its purification during production in an ion exchange column; however, no similar method for purifying NFPA has been discovered.

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Section X. (C) SUMMARY

(U) An adiabatic calorimeter was shown to be an accurate and convenient apparatus for determining the rate of thermal decomposition as a function of temperature for propellant and propellant ingredients. Small changes in purity of ingredients or various additives often made significant changes in the adiabatic heating rate without making noticeable changes in the results of the DTA, vacuum gas evolution, or small-scale fissuring tests.

(C) Adiabatic decomposition tests have shown that one thermal stability problem of RH-SB-type propellant is closely related to the HPMA-HMDI crosslinking system. Small-scale fissuring test results have demonstrated the superiority of an acrylic acid/diepoxide crosslinking system (RH-SE-type propellant) for prepolymer-based propellants, and the HPMA-HMDI crosslinking system (RH-SB-type propellant) has been abandoned. Since more recent studies with various RH-SE-propellant formulations have demonstrated the strong influence of high temperature mechanical strength on propellant fissuring behavior, a portion of the poor fissuring performance of RH-SB-type propellants perhaps can be attributed to its low mechanical strength at elevated temperatures. Significant improvements in propellant ingredients and copolymer manufacturing techniques which resulted in improved high temperature properties have come about since the preliminary study of RH-SB-type propellant. Hence, additional work on RH-SB-type propellant using current ingredients and techniques may be justified.

(C) Small-scale and 2-in. cube fissuring studies have demonstrated that improved fissuring performance for typical TVOPA/NFPA propellants can be obtained by coating the AP with Alon-C, a finely divided aluminum oxide.

(C) Comparison of the adiabatic heating rates for numerous samples of TVOPA with corresponding infrared analyses revealed a striking correlation between the heating rate and the absorption at 5.96μ in the infrared spectrum. TVOPA samples having high absorption at 5.96μ typically exhibit high adiabatic heating rates. A fluoriminocarbonate impurity is responsible for the 5.96μ absorption and can be greatly reduced in concentration by passing the TVOPA through an ion-exchange column containing Amberlyst-15 or by a sulfuric acid wash.

(C) The addition of a small quantity (1%) of either TVOP or FeAA in TVOPA results in a greatly increased adiabatic heating rate.

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TVOPA salted with small quantities of water, acetaldehyde (CH_3CHO) chloromethyl dioxolane, fluoroazoxy (NONF), or a fluoriminocyanide [5] impurity (which produces a peak at 6.23μ in the IR spectrum) produced little change in the decomposition rate. However, since the adiabatic decomposition tests began at a temperature of 250°F , the volatile additives (such as water) may have evaporated from the test samples before they contributed significantly to the decomposition.

(C) The use of FeAA curing catalyst in RH-SE-103 propellant decreases the time-to-fissure for 2-in. cubes stored at 80°C . Since this discovery, FeAA has no longer been used in RH-SE-103 propellant.

(U) Time-to-fissure for propellant can be increased by increasing the high temperature tensile strength. Use of copolymer manufactured by an incremental addition process [3] is an effective means for increasing high temperature strength of RH-SE-103 propellant and, hence, the time-to-fissure. Use of the incremental addition process, which is used to control molecular weight, is not limited to the copolymer for RH-SE-103 propellant; improved propellant properties and longer times-to-fissure should be obtainable with propellants made from a variety of copolymer systems.

(C) The absorption of moisture from the environment greatly reduces the time-to-fissure for TVOPA/NFPA propellant. In fact, 2-in. cubes of RH-SE-103 propellant stored at 100% relative humidity and ambient temperature for 12 days fissured severely during the ambient temperature storage. Similar cubes stored at 50% relative humidity for 12 days fissured in approximately one-fifth the time required for cubes which were placed in the ovens directly after delivery. Cubes stored for 50 days at ambient temperature and 0% relative humidity showed no reduction in time-to-fissure at 80°C . These tests indicate dramatically the importance of desiccating and sealing rocket motors directly after removal from the curing ovens.

(U) The storage of RH-SE-103 propellant in the presence of n-butyl ferrocene vapors resulted in serious degradation of the propellant mechanical properties.

(U) Fissuring studies using temperatures of 60° , 70° , 80° , and 90°C and cube sizes ranging from 1 to 4 in. have revealed cube dimensions which would never fissure at various temperatures. These data have been used to formulate a model for predicting useful

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propellant shelf life at service temperatures. The model and predictions of service life based on it are covered in a separate report [1].

(C) Sparging of propellant binder at 70°C with dry nitrogen is an effective method for removing small quantities of volatile impurities such as water and ethyl acetate. Even small amounts (less than 1%) of ethyl acetate act as an effective plasticizer in RH-SE-103 propellant, reducing strength while increasing elongation.

(C) Preliminary adiabatic decomposition tests of copolymer containing a 96/4 weight ratio of geminal NFPA/AA exhibited heating rates which were remarkably lower (by a factor of 150) than those of copolymer made with vicinal NFPA. When the geminal copolymer was combined with TVOPA, the adiabatic heating rate was lower than that for the corresponding binder containing vicinal copolymer, but the improvement was quite modest. Since two-thirds of the binder is TVOPA plasticizer, perhaps further improvements to binder thermal stability could be realized by replacing TVOPA with a geminal plasticizer. In fissuring tests, 2-in. cubes of propellant made from geminal copolymer have withstood over 2800 hr at 80°C without fissuring. However, propellant batches using incremental addition vicinal copolymer have performed equally as well in the 2-in. cube fissuring test at 80°C. At 90°C, better fissuring performance has been observed for cubes containing geminal NFPA. A limited supply of geminal ingredients will preclude extensive investigation in the foreseeable future.

(C) The rapid reaction of vicinal NF compounds with strong bases has been established in many synthetic and kinetic studies. The effect of water on cube fissure-times and of ethylene glycol on adiabatic heating rates presented indicate that slow reactions of the type often associated with ingredient incompatibility occur even with very weakly basic materials. Although not often thought of as bases, such compounds as water, alcohols, and salts of strong bases with weak acids (e.g., NaF, Na₃PO₄, etc.) exhibit the detrimental behavior typical of bases with vicinal NF compounds. Both dehydrofluorination and subsequent nucleophilic reactions which attach the base to the vicinal NF molecule are important.

(C) The incompatibility of FeAA and n-butyl ferrocene is thought to be the result of oxidation-reduction reactions or acid catalysis, rather than the general base action of water and alcohols.

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(C) The thermal stability of TVOPA/NFPA propellants has been increased by about two orders of magnitude as a result of these studies. RH-SE-103 propellant can now be made routinely with stability judged adequate for world-wide Army requirements. Further improvements using the incremental addition process can be achieved, and further improvements using geminal ingredients are still being studied.

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Appendix (C) EXPLANATION OF TABULATED VALUES FOR INFRARED SPECTROMETER ANALYSIS [4] (U)

(U) Absorbance (A) is defined as $\log_{10}(100/\%T)$ where (%T) represents percent transmittance. Absorbance, being a logarithm, has no real units. $A = 1.0$ —that is, $\log_{10}(100/\%T) = 1.0$ —is called one absorbance unit for convenience.

OH(%) - (C) Alcohols absorb at 2.78μ . Although ethyl alcohol is no longer thought to be present in TVOPA, the tabulated value is obtained from a calibration curve of absorbance versus weight percent ethyl alcohol in control samples of chromatographed TVOPA.

C=C(%) - (C) TVOP has absorptions at 6.10μ and 6.18μ . The (Double bonded carbon) 6.10μ band was chosen for C=C analysis because the stronger 6.18μ band is overlapped by a fluorimino-cyanide band. Results are reported as weight percent TVOP from a calibration curve, although partly saturated material is more likely present than TVOP.

NONF(%) - (C) The fluoroazoxy group ($\overset{\text{O}}{\underset{\uparrow}{\text{N}}}=\text{NF}$) has absorption at 6.60μ , and NONF is reported as weight percent of mono-NONF, penta NF_2 "TVOPA." The tabulated value is obtained from a calibration curve of absorbance versus weight percent $(\text{NONF})(\text{NF}_2)_5$ in pure TVOPA.

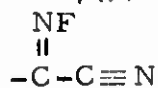
5.78μ - (C) Although this peak can be assigned with confidence to the carbonyl group ($-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-$), there appear to be several species which contribute. Acetaldehyde ($\text{HC}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$) is one of these; carbonates ($-\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-$), probably cyclic, are also likely. Since no single compound is responsible, results are reported in absorbance units.

5.96μ - (C) Fluoriminocarbonate ($-\text{O}-\overset{\text{NF}}{\underset{\parallel}{\text{C}}}-\text{O}-$) groups are responsible for this absorption. No standard curve is available, since these compounds are unstable and

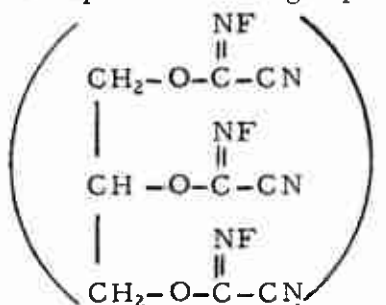
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difficult to separate. Results are reported in absorbance units.

6.23 μ (%) - (C) Fluoriminocyanide is reported as weight percent tris



fluoriminocyanide,



The tabulated value is obtained from a calibration curve of absorbance versus weight percent of pure

$\begin{array}{c} \text{NF} \\ || \\ \text{C}-\text{CN} \end{array}$ in pure TVOPA.

6.40 μ - (U) The origin of this rarely seen peak is not known, although nitro or nitrite groups are suspected. Measurement is reported in absorbance units.

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(C) GLOSSARY

AA	acrylic acid
Al	aluminum
AP	ammonium perchlorate
FeAA	ferric acetylacetonate
HMDI	hexamethylene diisocyanate
HPMA	3-hydroxypropyl methacrylate
NFPA (geminal)	2, 2-bis(difluoramino)propyl acrylate
NFPA (vicinal)	2, 3-bis(difluoramino)propyl acrylate
NFPOH	2, 3-bis(difluoramino)-1-propanol
NONE	fluoroazoxy
PPAA	NFPA/AA copolymer
RH	relative humidity
TCP	tricalcium phosphate
TEGDN	triethylene glycol dinitrate
TP	TVOPA/NFPA - copolymer mixture
TVOP	1, 2, 3-tris(vinyloxy)propane
TVOPA	1, 2, 3-tris[1, 2-bis(difluoramino)ethoxy] propane

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DOCUMENT CONTROL DATA - R & D		
<small>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</small>		
1. ORIGINATING ACTIVITY (Corporate author) Rohm and Haas Company Redstone Research Laboratories Huntsville, Alabama 35807		2a. REPORT SECURITY CLASSIFICATION Confidential
		2b. GROUP 4
3. REPORT TITLE THERMAL STABILITY OF SOME NF PROPELLANTS (U)		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)		
5. AUTHOR(S) (First name, middle initial, last name) Edwin L. Allen		
6. REPORT DATE December 1967	7a. TOTAL NO. OF PAGES 73	7b. NO. OF REFS 5
8a. CONTRACT OR GRANT NO. DAAH01-67-C-0655 8b. PROJECT NO. DA-01-021-AMC-11536(Z)	8c. ORIGINATOR'S REPORT NUMBER(S) Technical Report S-126	
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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U. S. Army Missile Command Redstone Arsenal, Alabama 35809	
13. ABSTRACT (C) The efforts of these Laboratories in evaluating and improving the thermal stability of high energy NF propellant based on NFPA and TVOPA are summarized. Test methods are briefly described. Sufficient experimental results are included to demonstrate significant improvements which were achieved. Methods which led to these improvements are described; these include the use of an acrylic acid-diepoxy curing system, purification of TVOPA in an ion-exchange column, inclusion of Alon-C ¹ (finely divided aluminum oxide) as a coating for ammonium perchlorate, omission of FeAA curing catalyst, and elimination of volatile contaminants from the binder. The importance of storing propellant in a dry environment and the effect of high temperature mechanical strength on cube fissuring behavior are shown. ¹ Trademark of Cabot Corporation, Boston, Mass.		

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14.	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	PROPELLANT THERMAL STABILITY, PROPELLANT THERMAL DECOMPOSITION, Solid Propellant, Stability Test, Propellant Shelf Life						
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	each transmittal to foreign governments or foreign nationals must have prior approval of Headquarters, U. S. Army Missile Command, Redstone Arsenal, Alabama 35809.						

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